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JOURNAL

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Optical Rotation. By H. LANDOLT (*Liebig's Annalen*, clxxxix, 241—337).—First Communication.—The author gives a lengthy historical sketch of the whole of the subject, from which he shows that almost all the determinations which have hitherto been made of the rotatory powers of substances in a state of solution are worthless, since little or no attention was paid to the degree of concentration, or to the nature of the inactive solvent. He has endeavoured to derive the power of rotation of a pure substance from that which it possesses in a state of solution, and so far has arrived at very satisfactory results for those bodies of which a solution can be obtained, containing over 50 per cent. of the pure material. For the methods employed the original paper must be consulted. From the results obtained with camphor, turpentine, ethyl tartrate, and nicotine dissolved in various solvents, among which were water, ethyl and methyl alcohols, acetic acid, benzene, dimethyl-aniline, ethyl acetate, and ethyl monochloracetate, the following conclusions are drawn:—

1. The specific rotatory power of an active body undergoes, not a sudden, but a gradual change on increasing dilution with an optically indifferent liquid. Whether the rotation is increased or diminished depends on the nature of the active substance; turpentine and ethyl tartrate, with various solvents, always show an increase, while nicotine and camphor always show a decrease of specific rotation. On the same active substance increasing amounts of various solvents exert a very different influence as to degree.

2. From the specific rotatory powers of a number of solutions of the same active body in different solvents, that of the pure substance can be calculated; and the same result is obtained whatever may be the indifferent solvent employed.

T. C.

Photoelectricity of Fluor Spar. By W. HANKEL (*Ann. Phys. Chem.* [2], ii, 66—83).—In investigating the thermoelectrical phenomena of crystals, the author was led to expect that since some crystals of fluor spar from Weardale, Durham, exhibited very strong fluorescence and phosphorescence, they might also exhibit electrical phenomena when exposed to light. His expectation was fully confirmed. On exposing a crystal to light, not only was its surface electrified, but the electrification was much stronger than that exhibited when the crystal was heated. For instance, a blue-violet crystal from Weardale was immersed in copper filings with one face exposed, and kept for some time at a temperature of 95° C. A short time after it began to cool, the face exhibited an electrification indicated by + 2 divisions of the electrometer used. On exposing the crystal to sunshine, the electrification was indicated by −23 divisions; and on exposure to diffused daylight for two hours, the electrification was −1·7 divisions. When exposed to the rays of the sun concentrated upon it by a large lens, the crystal lost the photoelectrical property, and did not regain it. Three other dark green Weardale crystals gave similar results. From experiments with coloured glasses, the author came to the conclusion that the effects are due to the so-called chemical rays. J. H. P.

Electrical Resistance of Flame. By E. HOPPE (*Ann. Phys. Chem.* [2], ii, 83—94).—The resistances of various parts of the flames of an argand lamp, of a Bunsen's burner, and of a hydrogen jet were measured by passing a current between two fine platinum wires, fixed at measurable distances apart, in a horizontal line, and at different distances above the orifice of the flame. From his results the author concludes that with the same flame the hotter parts conduct better than the colder; that with different flames of the same kind, the larger the cross-section the greater the conductivity, and that when salts are burned in the hydrogen flame, the conductivity is increased. The resistance of a given part of the flame is the same (within the errors of experiment) for the currents from three and four Bunsen's cells, from which the author considers that Ohm's law holds good for gases.
J. H. P.

Electrochemical Action at an Anode of Aluminium. By W. BEETZ (*Ann. Phys. Chem.* [2], ii, 94—100).—The author had remarked in a previous paper that the oxygen given up on the electrolysis of dilute sulphuric acid was too small (sometimes as much as 10 per cent.) when an aluminium anode was employed. He therefore made some experiments to determine the cause. The oxygen liberated from the sulphuric acid was either free, when it was collected on a eudiometer tube, or it entered into combination with the aluminium. By increasing the surface of the aluminium plate and the strength of the current, the oxygen was given off much more rapidly, and the deficit was then found to be much smaller, and ultimately it disappeared. This is explained by the fact that when the oxygen is given off slowly, it is partly dissolved by the surrounding liquid, and then ultimately escapes into the air. When, however, the decomposition is more rapid, the bubbles are so large that they rise up into the eudiometer tube over the anode, before the liquid has time to dissolve an appreciable quantity. J. H. P.

Chastaing's New Theory of the Chemical Action of Light. By HERMANN W. VOGEL (*Deut. Chem. Ges. Ber.*, x, 1638—1644).—This paper—which is not adapted for abstraction—is a refutation of a theory of the action of light recently published by Chastaing (*Ann. Chim. Phys.*, xi, 145). J. R.

A New Method of Determining Temperatures. By E. DRAGOUMIS (*Deut. Chem. Ges. Ber.*, x, 1648).—The method consists in using two thermometers, one at a higher the other at a lower temperature than that of the body under examination. On bringing the two thermometers into contact with the body, the mercury-column falls in one and rises in the other. The point at which the columns coincide is the true temperature of the body, supposing the thermometers to be accurate. J. R.

A New Apparatus for the Determination of High Melting Points. By R. ANSCHÜTZ and G. SCHULTZ (*Deut. Chem. Ges. Ber.*, x, 1800—1801).—This apparatus consists of an ordinary flask, into the neck of which is sealed a test-tube of tolerably wide bore, reaching nearly to the bottom of the flask. The shoulder of the flask is at one point drawn out into a tubulure, into which a small bent tube is fitted previously to an experiment. When the apparatus is not in use, a tube containing calcium chloride may be inserted. The flask is half filled through the tubulus with concentrated sulphuric acid or molten paraffin. To determine the melting point of a substance a small quantity is introduced into a capillary tube in the usual way, and the latter brought, together with a thermometer, into the test-tube. Heat is applied, and the melting point observed, precisely as in the ordinary method. The chief advantage of the apparatus, besides simplicity of construction, consists in the fact that the substance being heated in a bath of air instead of a liquid, absolute uniformity of temperature is secured. Further, no inconvenience is caused by the escape of fumes of sulphuric acid, which are entirely condensed within the upper part of the flask. The authors append the results of a series of observations of melting points taken by means of this apparatus, which leave nothing to be desired in point of accuracy. C. F. C.

Regularity in Melting Point of Homologous Compounds. By A. BAEYER (*Deut. Chem. Ges. Ber.*, x, 1286).—On comparing the melting points of acids of the acetic and oxalic series, it is noticeable that an acid containing an uneven number of carbon-atoms melts at a lower temperature than the one containing one atom of carbon more; the melting-point does not always rise as a homologous series is ascended, even if the number be compared in the series containing only even or odd numbers of carbon-atoms.

Even number of carbon atoms.	Melting point.	Odd number of carbon atoms.	Melting point.
4	180°	5	97°
6	148	7	103
8	140	9	106
10	127	11	108

and in the acetic series—

2	+ 17	3	Fluid at − 21
4	0	5	Fluid at − 16
6	− 2	7	− 10·5
10	+ 30	9	+ 12

Hence certain apparent exceptions to the usually supposed rule, that the melting-point rises as a homologous series is ascended, are really in consonance with the above empirical rule; thus synthetically prepared margaric acid melts lower than palmitic acid containing one carbon-atom more. C. R. A. W.

Calorimetric Researches. By A. Schuller and v. Wartha (*Deut. Chem. Ges. Ber.*, x, 1298).—The authors have described (*Deut. Chem. Ges. Ber.*, viii, 1011) an ice calorimeter differing from Bunsen's, in that the mercury sucked in is weighed instead of being measured by a scale, so that the influence of capillarity is avoided, and other advantages gained; in the present communication they briefly describe the results obtained by the use of this calorimeter for the estimation of the heat of combustion of hydrogen, fuller details being reserved for a longer paper. As unit of heat, they employ a "mean calory," *i.e.*, $\frac{1}{100}$ of the heat required to raise a gram of water from 0° to 100°. In order to calibrate their instrument in terms of the "mean calory," the following observations were made:—A glass vessel weighing 0·19158 gram, and holding 0·72445 gram of water, when cooled from 100° to 0°, caused (as the mean of 5 experiments) 1·1780 grams of mercury to be sucked in; whence, allowing 0·0580 gram of mercury as due to the contraction of the glass, 1·1200 gram is left to represent the contraction of the water. Hence per gram of water cooling from 100° to 0°, 1·5442 grams of mercury is sucked in, or 0·015442 gram of mercury represents a "mean calory." Notwithstanding the small quantities operated with, necessitating weighings to a hundredth of a milligram, the authors consider this result to be correct within one-thousandth of the amount; the value of the unit taken exceeds that of the ordinary calory (heat required to raise a gram of water from 0° to 1°) being 1·11 * times larger, according to Bosscha's corrections deduced from Regnault's data; Bunsen's experiments give 0·01541 gram of mercury per "mean calory." The difference between this value and that of the authors may be due to difference in the weighing-correction, as it is not stated whether Bunsen's weights were reduced to a vacuum or not; on the other hand, the value reckoned from Bunsen's determination of the sp. gr. of ice (0·91674), and Reg.

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* Query, 1·011 times larger.

nault's of the latent heat of fusion of ice (79·25) is 0·01573 gram of mercury per mean calory.

On burning electrolytic oxygen in an atmosphere of electrolytic hydrogen in a glass reservoir in the cavity of the ice calorimeter, the relation between the heat developed and the amount of materials consumed is readily deduced by weighing the water produced and the mercury sucked in to the calorimeter. In this way the following values were obtained in four experiments:—

	Grams of mercury sucked in per gram of hydrogen burnt.	Mean calories evolved.
	526·980	34126·8
	526·829	34116·9
	527·010	34128·7
	527·064	34132·1
Average..	526·971	34126·1

Von Than has recently found (*Deut. Chem. Ges. Ber.*, x, 947) the value 34040 calories; if this number be multiplied by $\frac{0·01541}{0·015442}$, (the ratio of the different values of mercury per mean calory found by the authors and by Bunsen, whose value was employed by Von Than), the result is 33971, or about 0·45 per cent. less than the above mean value. Andrews' well known researches, when recalculated to mean calories, give a yet smaller value, 33534; whilst J. Thomsen's and Favre and Silbermann's number (similarly reduced) are respectively 33633 and 34095, the values found by the authors being thus the highest.

In order to calculate the "affinity" between oxygen and hydrogen at the pressure 760 mm., and at a temperature, such that not only the materials employed, but also the product, steam, are perfect gases,* the following formula is employed:—

$$E = 34126 + M_1 - (M_2 + M_3),$$

when E is the reduced affinity value required; M_1 the heat required to raise the oxygen and hydrogen under constant pressure from 0° to the temperature fixed upon; M_2 the heat corresponding to the alteration in bulk from (3 to 2) during combination (calculable from the mechanical equivalent of heat); and M_3 the heat evolved by the steam produced on cooling down from the temperature fixed upon to 0°. Thus taking the temperature to be 225·86°, the value of E is 28810·7 calories per gram of hydrogen burnt to steam, the pressure being 760 mm. throughout, and the oxygen, hydrogen, and steam being all supposed to be at 225·86°. C. R. A. W.

On the Temperature of Combustion. By M. BERTHELOT (*Ann. Chim. Phys.* [5], xii, 302—310).—Bunsen sought to determine the temperature of combustion of carbon monoxide and of hydrogen in oxygen, by burning the gaseous mixture in a closed vessel, and measuring the pressure P at the moment of combustion.

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* Compare Alder Wright on the Relations between Affinity and Structural Formulæ (*Phil. Mag.* [4], xlviii, 401 (in abstract, this *Journal*, 1875, 228).

If Q = the temperature of combustion, C specific heat of the products of combustion, C′ mean specific heat of the mixed gases between 0° and t, k fraction of gas which has entered into combination, g theoretical condensation, and a = the mean specific heat for constant volume of the combining gases, and b that of the products of combustion, then (1) $t = \frac{kQ}{C'}$. (2) $P = P_0(1-k + kg)(1 + at)$.

$$(3)\ C' = (1-k)a + kb. \qquad (4)\ t = \frac{kQ}{(1-k)a + kb}.$$

$$(5)\ \frac{P}{P_0} = (1-k+kg)\left[1 + \frac{a\,kQ}{(1-k)a + kb}\right].$$

In order to solve the problem Bunsen assumes that the specific heat of the combining gases, a, and that of the combined gases, b, are constant quantities, independent of temperature and pressure. This hypothesis is incorrect, as the specific heat of carbon dioxide and of aqueous vapour varies rapidly with the temperature. The experiments prove neither the degree, nature, nor even the existence of dissociation. The two limits which must include the temperature of combustion can be calculated from Bunsen's data. From equation (2) it follows that (6) $t = 273\left(\frac{P}{P_0}\frac{1}{1-k+kg} - 1\right)$. The fraction of combined gas at the moment of explosion is between zero and one for a mixture of equivalent proportions of oxygen and carbon monoxide or hydrogen, between zero and m for a mixture containing $1 - m$ volume of inert gas. By replacing k successively by zero and one, or by zero and m, the two limits are obtained.

The following table compares Bunsen's results with the limits calculated by Berthelot:—

Combustible mixture in volumes.	$\frac{P}{P_0}$	t(Bunsen).	t'—t'' (Berthelot).
$\frac{2}{3}CO + \frac{1}{3}O$	10·78	3172°	2612—4140°
$\frac{2}{3}CO + \frac{1}{3}O + 0·1079\ O$	9·05	2558°	2198—3066°
$\frac{2}{3}CO + \frac{1}{3}O + 1·0861\ O$	7·86	2117°	1875—2280°
$\frac{2}{3}CO + \frac{1}{3}O + 1·2563\ N$ (air)	7·73	2084°	1838—2203°
$\frac{2}{3}CO + \frac{1}{3}O + 3·1629\ CO$	4·79	1146°	1034—1150°
$\frac{2}{3}H + \frac{1}{3}O$	9·97	2854°	2449—3809°
$\frac{2}{3}H + \frac{1}{3}O + 1·2599\ N$	7·49	2024°	1715—2126°

W. C. W.

Experiments on Evaporation. By G. BAUMGARTNER (*Wien. Akad. Ber.*, lxxv, 313—319).—The following results were obtained by measuring the rate of evaporation in different gases of ether, alcohol, carbon disulphide, and chloroform. In each case the rate of evaporation of the liquid in air is taken as unity:—

Rate of evaporation in air.	H.	Coal gas.	CO_2.
Ether .... ≐ 1	2·22	1·50	0·81
Carbon disulphide = 1	3·35	1·60	0·81
Chloroform ..... = 1	3·65	1·69	0·64
Alcohol .... = 1	3·58	1·80	—

These experiments confirm Stefan's theory of evaporation (this *Journal*, xxvii, 529), according to which the value of the coefficient of diffusion of a vapour, and consequently the rate of evaporation of the liquid, depends on the nature of the gas in which the diffusion takes place. W. C. W.

Explanation of the Experiments of Dufour and Merget upon the Diffusion of Gases. By A. KUNDT (*Ann. Chem. Phys.* [2], ii, 17—24).—Experiments have been made by Dufour, Merget, and others, which at first sight do not seem in accordance with Graham's law of gaseous diffusion. The author has repeated the experiments with the hope of reconciling them with that law. Merget's arrangement is as follows :—An ordinary porous cell thoroughly saturated with water is closed at the open end by a stopper, through which passes a glass tube either connected with a manometer or leading under water, where an inverted gas-collecting tube is placed over its end. When the porous cell is heated, we might expect that the damp and therefore lighter air would diffuse outwards more rapidly than the dry and heavier air would diffuse inwards. It is found, however, that when a sufficient heat is applied, a large quantity of air is expelled from the cylinder into the collecting tube, sometimes many times the volume of the cylinder, showing that the diffusion from without inwards is far greater than that from within outwards. The author of this paper gives the following explanation of this fact in accordance with Graham's law. Since the vapour will diffuse out more rapidly than the air will diffuse in to take its place, a partial vacuum will be formed inside the cylinder; but the air from outside will then diffuse in and restore the inside pressure to its original amount. Now, however, fresh evaporation will take place from the surface of the cell, and we shall have an inside pressure greater than that without by the amount of pressure of the aqueous vapour within. Some of the air will therefore be expelled from the cell into the collecting tube. The process will then be repeated, and we shall have air expelled from the cell till its walls become dry. J. H. P.

Heat of Absorption of Hydrogen Chloride by Water: a Lecture Experiment. By A. CHRISTOMANOS (*Deut. Chem. Ges. Ber.*, x, 1645—1647).—The caoutchouc stopper of a glass cylinder is arranged to carry two similar thermometers, one of which has its bulb covered with filter-paper moistened with water, and also a test-tube, likewise covered with filter-paper, and containing carbon bisulphide heated to about 40°. On introducing the arrangement into a cylinder of dry hydrogen chloride, the coated thermometer rises rapidly to 70°, the other remaining unaffected, whilst the carbon bisulphide speedily begins to boil. If before the experiment the vapour of the bisulphide is ignited at the mouth of the test-tube, which should project through the stopper, the flame increases greatly in size when the liquid begins to boil, and thus becomes visible at some distance.

When the paper is moistened with alcohol instead of water, the temperature rises to 51° only. With concentrated ammonia instead of water the temperature rises to 87°.

A thermometer covered with moistened paper and plunged into dry ammonia gas shows a rise of temperature of 8° or 10° at most.

J. R.

Observations on the Mechanism of Chemical Reactions. By M. BERTHELOT (*Ann. Chim. Phys.* [5], xii, 312—318).—Slightly moist haloïd salts absorb ozone at the ordinary temperature, forming chlorates, bromates, and iodates. By the union of oxygen with potassium iodide to form iodate, + 44·1 heat-units are evolved; to oxidise the chloride and bromide, 11·0 and 11·1 heat-units would be absorbed. Free oxygen does not act on potassium chloride or bromide, but it unites with dry potassium iodide at a temperature between 400—450°, forming potassium iodate and a small quantity of tri-iodide; the residue has an alkaline reaction. Perhaps the following change take place:— $4KI + O_4 = KIO_3.K_2O + KI_3$. This basic iodate has not yet been isolated.

The union of I with O to form I_2O_5 should evolve +46·8 heat-units, but the two elements will not combine. In the same way $SO_2 + O = SO_3$ should give 34·4, but the dry gases will not act on each other. When sulphur burns in oxygen, a certain amount of trioxide is always formed.

Dry arsenious oxide will not unite with oxygen; in solution it oxidises evolving 78·4. Oxidation does not take place at the ordinary temperature except in presence of platinum-foil. At 100° oxidation goes on slowly; much more rapidly in contact with platinum-foil. A solution of potassium arsenite gives off 134·6 heat-units on oxidation to arsenate, *i.e.*, almost twice as much heat as is set free when the same weight of oxygen unites with arsenious acid. W. C. W.

Influence of Pressure on Chemical Phenomena. By M. BERTHELOT (*Ann. Chim. Phys.* [5], xii, 310—311).—When a mixture of sulphuric acid and zinc is subjected to great pressure, the evolution of gas diminishes but does not cease. The chemical affinity is not modified; but the abatement is due to the surface of the metal being covered with a film of gas, whilst the acid immediately surrounding the zinc is saturated. W. C. W.

Relative Affinities of Hydrogen and Carbon Monoxide for Oxygen. By AUG. HORSTMANN (*Deut. Chem. Ges. Ber.*, x, 1626—1630).—Bunsen's experiments on the amounts of hydrogen and carbon oxide burnt, when mixtures of these gases are detonated with a quantity of oxygen insufficient for their complete combustion, led him to conclude that the proportion by volume of the products (water-vapour and carbon dioxide) may always be expressed by small whole numbers, and that, consequently, while the proportion of hydrogen in the original mixture increases regularly, the proportion of the products of combination alters by leaps.

E. v. Meyer afterwards made similar experiments (*Journ. pr. Chem.* [2], x, 273; xiii, 121; *Journ. Chem. Soc.*, 1876, ii, 40), the results of which appeared to him to confirm those obtained by Bunsen.

The author of the present paper thinks that Bunsen's experiments were too few in number to establish the conclusion based upon them, and that the results of Meyer's experiments are not sufficiently definite to have any real bearing on the question. The results of his own experiments on the subject are thus summed up:—

1. When carbon oxide is detonated with increasing quantities of water-gas, as in Bunsen's experiments, the proportion of water-vapour to carbon dioxide in the products increases constantly. Whilst the proportion of hydrogen to carbon oxide increases from 0·25 : 1 to 2·33 : 1, or, in other words, whilst from 20 to 70 per cent. of the combustible gases is burnt, the proportion of the products (H_2O : CO_2) varies from 0·8 : 1 to 4·5 : 1.

2. When a mixture of hydrogen and carbon oxide is detonated with increasing quantities of oxygen, as in Meyer's experiments, water-vapour and carbon dioxide are likewise formed in constantly increasing proportions.

The division of oxygen between the two combustible gases does not, therefore, take place in the manner supposed by Bunsen.

3. With moist gases less hydrogen and more carbon oxide are burnt than when the gases are dry. On the other hand, when carbon dioxide is present in the mixture before detonation, more hydrogen and less carbon oxide are burnt. [In the latter case some carbon dioxide would most probably be reduced by hydrogen in the detonation, and the proportion of carbon oxide burnt would, consequently, appear to be less (J. R.).]

4. In experiments with mixtures of hydrogen and carbon oxide, the proportion of the products of combustion (H_2O : CO_2) varies in a peculiar manner. With increasing quantities of oxygen, this proportion increases at first, attains a maximum when 30—35 per cent. of the combustible gas is burnt, and then gradually decreases towards the limit that would be reached if the whole of the gases were burnt, *i.e.*, towards the proportion of hydrogen and carbon oxide before detonation. Thus, for instance, in a mixture of hydrogen and carbon oxide containing 54·6 per cent. of hydrogen, the proportions of the products were successively 3·83, 4·09, 4·18, 3·96, 2·80, and 2·09 : 1, when the amounts of the gases burnt were respectively 21·7, 29·1, 34·9, 41·7, 53·9, and 66·2 per cent. of the whole.

5. The law according to which the oxygen is divided between the combustible gases may be expressed thus:—The proportion of the resulting water-vapour to the resulting carbon dioxide is equal to the proportion of the unburnt hydrogen to the unburnt carbon oxide, multiplied by a co-efficient of affinity which is independent of the proportion of the combustible gases, but which varies with the relative quantities of oxygen added. According to the author's experiments, the co-efficient of affinity varies between 4·0 and 6·4 when between 20

and 70 per cent. of the combustible gases is burnt, the maximum co-efficient coinciding with the combustion of 30—40 per cent. of the gases. In other words, the proportion of water-vapour to carbon dioxide was found to be from 4·0 to 6·4 times as great as the proportion of hydrogen to carbon oxide in the residue unburnt. Hence, relatively more hydrogen than carbon oxide is burnt in all cases: the affinity of oxygen for hydrogen is greater than for carbon oxide.

6. The variability in the co-efficient of affinity is due to the circumstance that the physical conditions of the reaction vary with the relative quantities of oxygen present. With equal quantities of oxygen the co-efficient remains constant, not only when the proportion of hydrogen to carbon oxide is altered, but also when the unconsumed portion of the combustible gases is replaced, partially or entirely, by an indifferent gas of similar physical characters, such as nitrogen, although the proportion of unburnt gases to the products of combustion varies in both cases. J. R.

Quantivalence of Nitrogen. By A. LADENBURG (*Deut. Chem. Ges. Ber.*, x, 1634—1638).—The author showed in a former paper that there exist two isomeric compounds of the formulæ $N(C_2H_5)_3,C_7H_7I$ and $N(C_2H_5)_2C_7H_7,C_2H_5I$, distinguishable by their behaviour when distilled with hydriodic acid. The former compound, it was stated, breaks up, under this treatment, into triethylamine and benzyl iodide, whilst the latter undergoes no change.

The correctness of this conclusion has since been questioned by V. Meyer, who asserts that no reaction with hydriodic acid occurs in either case.

The author, having now again distilled triethylbenzyl-ammonium iodide with hydrogen iodide, and proved beyond a doubt the formation of benzyl iodide and triethylamine, maintains the strict correctness of the results formerly published. J. R.

Inorganic Chemistry.

Liquefaction of Oxygen. By RAOUL PICTET (*Chem. News*, xxxvi, 281).—This gas has been liquefied under a pressure of 300 atmospheres at the temperature produced by the rapid evaporation of liquid carbon dioxide in a vacuum. By a double circulation of sulphur dioxide and carbon dioxide, this latter gas was liquefied at a temperature of −65° and a pressure of 4 to 6 atmospheres. The liquid carbon dioxide was passed along a tube about 4 meters long, communicating with two air-pumps. When a vacuum is produced by these pumps the carbon dioxide solidifies. In the interior of the tube is a smaller one, through which passes a current of oxygen, produced in a strong vessel. The whole apparatus can stand a pressure of 800 atmospheres.

With this apparatus oxygen was liquefied at a pressure of about 300 atmospheres, a jet of liquid oxygen escaping from the tube when the pressure was taken off. C. W. W.

Liquefaction of Nitrogen Dioxide. By CAILLETET (*Compt. rend.*, lxxxv, 1017).—This gas was liquefied at a pressure of 104 atmospheres, and a temperature of $-11°$. It is still liquid at $+8°$ and 270 atmospheres.

Methane at 7° and a pressure of 180 atmospheres gives a cloudy appearance, similar to that produced when the pressure is suddenly taken off liquid carbonic acid. C. W. W.

On Iodine Chlorides, Iodine Bromide and Bromine Chloride, and their Reaction with Water. By W. BORNEMANN (*Liebig's Annalen*, clxxxix, 183—213).—The main results of the author's experiments are as follows:—

(1.) Pure iodine chloride, ICl, remains liquid in a sealed tube, but solidifies on opening the tube.

(2.) In presence of iodine trichloride the monochloride crystallises even in a sealed tube.

(3.) By distillation, and by long exposure to air, iodine chloride is partially decomposed into iodine and trichloride.

(4.) Iodine chloride is not soluble in water without decomposition; it dissolves in dilute hydrochloric acid without separation of iodine.

(5.) If iodine be suspended in water and chlorine be passed through the liquid, the greater the quantity of water present, the greater is the amount of chlorine required for complete solution of the iodine.

Complete conversion of the iodine into iodic acid is accomplished only when a minimum of 10 parts water to 1 part iodine is maintained. Iodic acid then separates out, and iodine trichloride may be obtained from the liquor.

(6.) Iodine bromide is a crystalline body resembling iodine; it may be distilled with partial decomposition; it dissolves in water with separation of but little iodine.

(7.) No hydrate of the composition $BrI.5H_2O$ exists.

(8.) Bromine chloride is a red-brown liquid, stable only at temperatures under $+10°$.

(9.) $BrCl + 5H_2O$ does not exist: the crystalline mass obtained by decomposing bromine chloride with water—if a true compound at all—is represented by the formula, $BrCl.10H_2O$. M. M. P. M.

Preparation of Iodine Trioxide. By J. OGIER (*Compt. rend.*, lxxxv, 957—959).—By the action of a mixture of ozone and oxygen on the vapour of iodine, an exceedingly light yellow dust is obtained in small quantities, which is decomposed by water, with formation of iodic acid and separation of iodine. It is very deliquescent, and when heated between 125—130°, decomposes into iodine and oxygen. Its analysis gives numbers corresponding with the formula, I_2O_3.

L. T. O'S.

Boric Acid. By M. L. DIEULAFAIT (*Ann. Chim. Phys.* [5], xii, 318—354).—In complex saline solutions, the only trustworthy methods of detecting boric acid are by spectrum analysis and by the green colour imparted to a Bunsen's flame. A drop of the solution under examination is placed on a ball of magnesia, prepared by dipping a platinum wire in a saturated aqueous solution of magnesium chloride, drying the wire in the gas-flame, and repeating the operation until a spongy mass of magnesia four millimeters in diameter is obtained. This ball impregnated with the solution is heated in a non-luminous flame, which is examined through a spectroscope. In this way $\frac{1}{400,000}$ grm. of boron can be detected.

A mixture of the substance with strong sulphuric acid held on the loop of a thick platinum wire imparts a distinct green colour to the flame, when $\frac{1}{1,000,000}$ grm. of boron is present. The wire should be placed from two to four millimeters from the outer edge of the visible flame, so that the temperature is not high enough to volatilize the sodium salts.

Sea-water contains appreciable quantities of boric acid, and on evaporation the boric acid collects in the last mother-liquors. In the Stassfurt salt beds boric acid occurs in the top layers with magnesium chloride and other deliquescent salts. The Mediterranean contains 0·2 grm. of boron or 1·73 grms. of sodium borate per cubic meter.

The saline deposits of the trias and tertiary formations have been formed by the evaporation of sea-water; hence they must contain considerable quantities of boric acid. It is to these salt-beds of the tertiary formation that the boric acid in the Tuscan lagoons owes its origin, and not to the action of steam on boron nitride or sulphide, as was formerly supposed. Volcanic heat volatilizes the water in the salt beds, and partly decomposes the magnesium chloride with which the boric acid is probably associated; hydrochloric acid is thereby set free, which in its turn liberates boric acid. W. C. W.

Synthesis of Ultramarine. By J. F. PLICQUE (*Compt. rend.* lxxxv, 749—752).—A silico-aluminate of sodium prepared by mixing equivalent parts of sodium silicate and sodium aluminate in solution, was heated in a current of carbon disulphide vapour, when a yellowish-white compound was obtained, which rapidly absorbed oxygen from the air, with evolution of sulphuretted hydrogen, the colour changing to blue.

This compound heated in a current of sulphur dioxide absorbed large quantities of it, free sulphur separating out. The blue compound thus obtained contained 41·3 per cent. of sodium sulphate, but no free sulphur.

The author's conclusions are (1) that ultramarine contains no nitrogen; and (2) ultramarine-blue is a compound of sulphur dioxide with sodium and aluminium.

The sulphur in the carbon disulphide replaces part of the oxygen in the silico-aluminate of soda, forming sodium sulphide, which, with sulphur dioxide, forms sodium sulphate, with liberation of sulphur.

By substituting the corresponding selenium-compounds for those of sulphur, a red compound was obtained. L. T. O'S.

Nitroxylsilver, or Silver Hyponitrite. By W. ZORN (*Deut. Chem. Ges. Ber.*, x, 1306).—The author entirely corroborates the statements of Divers that silver hyponitrite, NOAg, is formed when sodium-amalgam acts on solution of potassium nitrate, and the product is neutralised with acetic acid and precipitated by silver nitrate. Divers did not obtain the silver salt perfectly pure, as shown by his analytical numbers, and by the greenish-yellow colour of his product; the author has obtained it quite pure by solution in dilute nitric acid, and careful neutralisation by ammonia: it then forms a pure yellow substance soluble in nitric acid and in ammonia, and capable of being dried in a vacuum over sulphuric acid without decomposition; when dry it undergoes no change at 100°. The yield is about 15 per cent. of the nitrate employed, about the same result being obtained if a nitrite be employed instead. Silver hyponitrite is readily acted on even in the cold by methyl, ethyl, normal propyl, normal secondary butyl, tertiary butyl, and hexyl iodides, silver iodide being formed with evolution of heat; the products of these actions are under investigation. C. R. A. W.

Amount of Water in Hydroauric Chlorides. By JULIUS THOMSEN (*Deut. Chem. Ges. Ber.*, x, 1633).—The author finds that this substance in the dry state, as obtained by drying the crystals over quick-lime, contains 4 mol. of water. Its formula is, therefore, $AuCl_4H + 4H_2O$. J. R.

Tin Phosphide. By S. NATANSON and G. VORTMANN (*Deut. Chem. Ges. Ber.*, x, 1459—1461).—The authors have analysed certain varieties of tin phosphide prepared by the following methods: (1.) By heating together glacial phosphoric acid, 3 parts; charcoal, 1 part, and tin 6 parts. (2.) By fusing together glacial phosphoric acid and metallic tin. (3.) By passing phosphorus vapour in a stream of hydrogen over melted tin; and (4.) By adding phosphorus to melted tin.

Prepared according to the above methods, the phosphide was silvery-white, of leafy crystalline structure, and soluble in hydrochloric acid with evolution of phosphuretted hydrogen.

The analytical results in each case are as follows:—

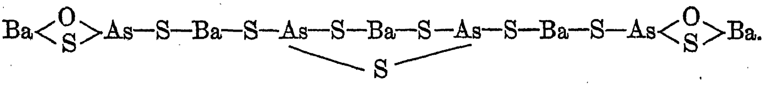
(1.) Sn 97·97, P 1·52, and 1·37 per cent.; when heated to redness in a current of hydrogen, a loss of 0·997 per cent. of phosphorus was estimated.

(2.) P 0·746, and 0·827 per cent. (3.) Sn 96·551. P 2·856. (4.) This variety resembled the preceding.

The two commercial varieties of the phosphide, which are also silvery-white and exhibit a leafy fracture, were found to contain: (No. 0) 95·904 per cent. Sn. (No. 1) 98·9 per cent. Sn.

C. F. C.

Barium Oxysulpharsenite. By L. F. NILSON (*J. pr. Chem.* [2], xvi, 93—96).—From the mother-liquors of barium sulpharsenite, $2BaS.As_2S_3 + 5H_2O$ (*J. pr. Chem.* [2], xiv, 48), the author obtains by boiling a yellow crystalling precipitate, to which he had formerly given the formula, $5BaS.2As_2S_3 + 6H_2O$. Further analytical results lead him to attribute to it the composition $5BaS.2As_2S_2O + 6H_2O$. This formula is also supported by the observation that from the mother-liquors a barium sulpharsenit-arsenate, $5BaS\left\{\begin{matrix}As_2S_3\\As_2S_5\end{matrix}\right. + 8H_2O$ separates out, owing its formation to that of the oxysulpharsenite, as by this the necessary sulphur is set free. The author attributes the following constitution to this oxysulpharsenite:—



$$\mathrm{Ba}{<}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{S}}{>}\mathrm{As{-}S{-}Ba{-}S{-}}\underbrace{\mathrm{As{-}S{-}Ba{-}S{-}As}}_{\mathrm{S}}\mathrm{{-}S{-}Ba{-}S{-}As}{<}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{S}}{>}\mathrm{Ba}.$$

Two analogous arsenic compounds are known, viz., the bisulpharsenic acid in the salt of Cloez, $K_2O.As_2S_2O_3 + 2H_2O$, and the bisulpharsenic acid, $As_2S_3O_2$ prepared by the author (*J. pr. Chem.* [2], xii, 297). P. P. B.

On the Atomic Weight of Molybdenum and certain Phosphomolybdates. By C. RAMMELSBERG (*Deut. Chem. Ges. Ber.*, x, 1776—1780).—Prior to his investigation of the phosphomolybdates, the author has made a determination of the atomic weight of molybdenum, by reduction of the anhydride to metal in a stream of hydrogen. The experimental number thus obtained was 96·18: molybdenum is therefore taken as Mo = 96.

Ammonium and Potassium Phosphomolybdate.—To the well known yellow ammonium salt and the corresponding potassium compound, the author assigns the formula: $3R'_2O.P_2O_5.22MoO_3.12Aq$.

By the action of a small quantity of potash-solution, the yellow potassium salt is converted into a white insoluble modification: $5K_2O.P_2O_5.15MoO_3$. On boiling the alkaline filtrate from this salt, a flocculent precipitate of $K_2Mo_3O_{10}$ is obtained.

By dissolving this compound in a small quantity of potash-solution and adding phosphoric acid, a salt is obtained in white shining prisms of the composition, $5K_2O.2P_2O_5.10MoO_3.20Aq$.

By fusing 1 mol. K_2CO_3 with $2MoO_3$, dissolving in water, and adding phosphoric acid to the solution, a compound crystallising in large colourless octohedrons is obtained. The formula of this salt,

$$3K_2O.P_2O_5.5MoO_3.7Aq,$$

exactly corresponds with that assigned by Zenker to the colourless compound obtained from the solution of the yellow ammonium phosphomolybdate in ammonia. C. F. C.

Osmium Oxysulphides. By E. VON MEYER (*J. pr. Chem.* [2], xvi, 77—86).—The author has shown that oxidised platinic sulphide is a hydrate of platinum sulphoxide, PtSO (*J. pr. Chem* [2], xiv, 1). He finds that by treating an aqueous solution of osmium tetroxide with sulphuretted hydrogen, a precipitate is formed, which, when suspended in water, and submitted to the further action of sulphuretted hydrogen, yields a loosely crystalline body, easily oxidised on exposure to air, and having the formula; $Os_3S_7O_5.2H_2O$. The oxidation of this body by air at 70—80° yields an unstable, odourless, and insoluble body, having the composition $(OsSO_3).3H_2O$. Further exposure to air yields osmium tetroxide. The presence of sulphur in these bodies renders the oxygen more easily removed than in osmium tetroxide, and produces a tendency to form hydrates, which the latter does not.

For the method of analysing these unstable bodies, the original paper must be consulted. P. P. B.

Mineralogical Chemistry.

Preparation of Orthose. By P. HAUTEFEUILLE (*Compt. rend.*, lxxxv, 952—955).—Potassium tungstate and aluminium silicate, when fused together between 900° and 1000°, give rise to a crystalline silicate, which resembles orthose in its chemical and physical properties. Its crystalline form resembles that of orthose, and its optical properties are those characteristic of bodies crystallising in the monoclinic system.

L. T. O'S.

Bowlingite, a New Scottish Mineral. By J. B. HANNAY (*Min. Mag.*, 1877, 154—157).—This mineral was found filling a slicken-sided fissure on the north side of the quarry, in the "Hill of Dun," at Bowling, on the Clyde, three miles east of Dumbarton. The rock called the "Hill of Dun," was described by Mr. Samuel Allport (*Trans. Geol. Soc.*, xxx, 558) as a brownish-black, or black crystalline, porphyritic dolerite, built up of distinct crystals of augite, olivine, and felspar. The ground-mass is rather finely crystalline, and consists of small crystals or grains of the above-mentioned constituents, together with numerous grains of magnetite. The plagioclase crystals are large, and enclose glass cavities and portions of ground-mass. Formation of serpentine after olivine is very distinct throughout this rock. The new mineral has a fine deep-green colour by transmitted light, and small crystals of olivine are present, thus showing it to be a secondary formation from olivine. Streak, light arsenic-green. Spec. gr. varying from 2·283 to 2·290. It is very soft, has a steatitic feeling, and a slight pearly lustre; is easily decomposed by boiling dilute acids (especially hydrochloric and sulphuric acids), gelatinous and slimy silica being left. This mineral was also found on the Cathkin Hills, near Glasgow. The author analysed samples from Bowling and Cathkin, with the following results, viz.:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	$CaCO_3$.	H_2O.	
Bowling No. 1 ..	34·32	18·07	3·65	6·81	9·57	5·14	22·70	= 100·26
,, ,, 2 ..	35·08	16·85	3·92	6·95	10·22	4·89	21·85	= 99·76
Cathkin No. 1 ..	35·66	15·09	5·22	7·02	12·41	5·02	19·89	= 100·31
,, ,, 2 ..	35·82	16·14	4·85	6·99	11·73	4·87	19·63	= 100·03

It is not easy to assign a formula to this mineral, on account of the quantity of calcium carbonate present. A further investigation is considered necessary, as an analysis of the *same* specimen, made by Mr. J. W. Young, differs completely from that of the author.

C. A. B.

New Minerals from the Collection in the University of Glasgow. By J. B. HANNAY (*Min. Mag.*, 1877, 149—153).—*Arsenargentite.*—Locality unknown. The first specimen examined by the author consisted principally of native arsenic, but enclosed in it were acicular crystals of a new mineral, which was found to have the following percentage composition, viz.:—

	Found.	Calculated.
Ag	81·37	81·20
As	18·43	18·80
	99·80	100·00

from which the formula, Ag_3As, is deduced, and the name proposed for it is *arsenargentite*. The crystals were apparently rhombic. Associated with the arsenic was crystallised quartz, of a rose-pink colour.

Plumbomanganite is a dark, steel-grey, somewhat crystalline mineral (having a bronze tinge, when weathered), with a spec. gr. of 4·01, and occurring in a "pocket" in gneiss, below a deposit of argentite. An analysis of this mineral furnished the following results, viz.:—

	Found.	Calculated.
Mn	49·00	49·62
Pb	30·68	31·13
S	20·73	19·25
	100·41	100·00

from which the formula, $3Mn_2S.PbS$, is obtained. It is easily oxidised by nitric acid, and slowly attacked by boiling hydrochloric acid and sulphuric acid.

Youngite.—Immediately below the silica on the last-named specimen were observed small pieces of a bright, crystalline, hard body, which was found to have the following percentage composition, viz.:—

	Zn.	Mn.	Pb.	S.	
Found..........	40·07	11·13	20·92	28·85	= 100·97
Calculated......	39·26	11·05	20·78	28·91	= 100·00

from which the formula, $6ZnS.2MnS.PbS$, is obtained. Spec. gr., 3·62. The larger portion of the mineral is made up of a substance resembling fractured cast-iron, of a very crystalline nature, and on analysis yielded the following percentages, viz.:—

	Zn.	Pb.	Mn.	Fe.	S.	
Found	38·46	24·22	6·93	2·83	27·50	= 99·94
Calculated....	37·81	25·01	6·64	2·71	27·83	= 100·00

the latter agreeing tolerably well with the formula, $6.ZnS\left\{\begin{array}{l}1·25\,Pb\\1·25\,Mn\\0·50\,Fe\end{array}\right\}S$.

Further analyses proved the mineral to have a constant composition as above. Spec. gr., 3·59. The author proposes to name it "Youngite," after the Director of the Museum of Glasgow University.

Note by Abstractor.—A microscopical examination and repeated analyses of the above-mentioned mineral appear to be desirable, in order to ascertain whether this supposed new mineral be not in reality a mixture of zinc-blende, alabandite (MnS), galena, and iron-pyrites. From the analysis given above, the constitution of this substance certainly appears to be as follows, viz. :—

Zinc-blende.	Galena.	Alabandite.	Iron-pyrites (FeS_2).
57·33	28·00	10·96	6·06 = 102·35

C. A. B.

Miargyrite and Kenngottite. By L. Sipöcz (*Liebig's Annalen*, clxxxviii, 343).—The author finds that *miargyrite* from Felsöbánya has the specific gravity, 5·322 to 5·273; after subtracting from the results of analysis minute quantities of copper and iron, and 4·01 per cent. of lead, and adding an equivalent quantity of silver, he finds that it agrees in composition well with the formula, $AgSbS_2$. *Kenngottite* was found to have exactly the same specific gravity (5·2918 to 5·3822), and contained the same elements; after subtracting traces of iron and copper, and calculating 1·76 per cent. of lead to silver, the analysis also agreed well with the formula, $AgSbS_2$. Both of these minerals, therefore, are really mixtures of true miargyrite (from Braünsdorf—Rose) or pure $AgSbS_2$, and the isomorphous zinckenite, $PbSb_2S_4$, the former greatly predominating. C. R. A. W.

Mineral Analyses. By C. Winkler (*J. pr. Chem.* [2], xvi, 86—93).—(1.) *Roselite.*—To this mineral, from analyses of the Schneeberg variety, the author gave (*J. pr. Chem.* [2], x, 191) the general formula $(AsO)''_2O_6R''_3 + 2H_2O$. Schrauf (*Monograph des Roseliths*, Wien, 1874) attributes to it the formula $(AsO)''_2O_6.R''_3 + 3H_2O$. From a special determination of the water in this mineral, by passing dry air over it heated to redness, and collecting the water in a calcium chloride tube, the author finds his original formula to be correct.

(2.) *Cobalt-spar.*—This mineral was found by A. Weisbach associated with roselite of the Daniel mine in Schneeberg, as a black, velvet-like mineral, the interior being of an erythrin-red colour. It has proved to be a cobalt carbonate, and from its crystalline form it must be placed next to sphærosiderite, and is a member of the calc-spar group.

(3.) *Bismuthosphærite.*—This name has been given to the mineral by A. Weisbach (*Jahrbuch f. d. Berg. u. Huttenwesen in Königreich Sachsen*, 1877), which is the old arsenious bismuth of Werner. Analysis proves it to be a carbonate, having the formula, $(BiO)'_2CO_3$.

(4.) *Uranocircite.*—The mineral, so named by Weisbach (*op. cit.*, 1877), is a species of uranite, found in "Falkenstein, in the Voigtland," and was regarded as a calcium-uranium phosphate. Analyses by Max Georgi and Uwao Imai, show it to contain barium, and that the formula is $BaO.2U_2O_3.P_2O_5 + 8H_2O$. P. P. B.

Ixolyte. By H. Weidel (*Wien. Akad. Ber.*, xxiv, 387—388).—This mineral occurs in the lignite of Gloggnitz, in the form of semifluid drops, which darken in colour and harden on exposure to the air.

Ixolyte, purified by solution in alcohol, yields pyrocatechin when fused with caustic potash.

W. C. W.

The Mineral Spring of O Tura, in Hungary. By H. WEIDEL and G. GOLDSCHMIEDT (*Wien. Akad. Ber.*, lxxiv, 391—393).—The temperature of this spring in summer is 10° C.; its specific gravity at 22·9° is 1·00107. The water turns litmus red, but after the carbonic acid has escaped, it has a strongly alkaline reaction. A considerable quantity of gas is given off by the spring; it contains 9·86 per cent. carbon dioxide, 86·51 per cent. nitrogen, and 3·42 per cent. oxygen.

10,000 parts of the water contain—

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	K_2O.
0·1402	0·0063	0·0374	2·4450	0·5560	0·0087

Na_2O.	SO_3.	Cl.	CO_2.	Total solids.
1·3327	0·0046	0·2879	10·8540	8·0490

also traces of phosphoric acid, ammonia, and organic matter.

W. C. W.

On some Mineral Springs in the Neighbourhood of Lake Laach. By R. BENDER (*Arch. Pharm.* [3], xi, 50—53).—The so-called Heilbrunnen spring is one of the most interesting mineral springs of the Brohl valley. Its water is quite clear, colourless, and rich in gas. It yields daily about 4,908 liters of water and 650 liters of gas (free carbonic acid). On allowing the water to stand in an open bottle, it becomes turbid, probably in consequence of the conversion of ferrous into ferric oxide, a circumstance which is often observed with water rich in ferrous carbonate. Fresenius recently found that 1,000 parts of this mineral water contains the following ingredients:—

K_2SO_4.	Na_2SO_4.	NaCl.	NaI.	NaBr.	$NaNO_3$.	$AlPO_4$.
0·09900	0·14763	1·41489	0·00001	0·00080	0·00046	0·00013

$NaPO_3$.	Li_2CO_3.	Na_2CO_3.	$(NH_4)_2CO_3$.	$BaCO_3$.	$SrCO_3$.	$CaCO_3$.
0·00018	0·00390	1·81999	0·00535	0·00006	0·00006	0·38275

					Carbonic acid.	
$MgCO_3$.	$FeCO_3$.	$MnCO_3$.	SiO_2.	Total.	Partly combined.	Free.
1·07420	0·02138	0·00031	0·22741	5·19851	1·49961	2·39334

Total = 9·09146.

The Stahlbrunnen spring at Wassenach is also situated in the Brohl valley. Its water has a pleasant taste. The spring gives 9,072 liters of water and 6,840 liters of free gas in 24 hours. The specific gravity of the water at 9·2° R. is 1·0027. 1,000 parts contain, according to Fresenius:—

K_2SO_4.	$KClO_3$.	$NaClO_3$.	$NaNO_3$.	$NaPO_3$.	$AlPO_4$.	Li_2CO_3.
0·05444	0·03575	0·00911	0·00102	0·00040	0·00045	0·00030

Na_2CO_3.	$(NH_4)_2CO_3$.	$BaCO_3$.	$SrCO_3$.	$CaCO_3$.	$MgCO_3$.	$FeCO_3$.
0·63123	0·00281	0·00009	0·00120	0·37582	0·70976	0·03630

			Carbonic acid.		
$MnCO_3$.	SiO_2.	Total.	Partly combined.	Free.	Total.
0·00269	0·04107	1·90244	0·81568	2·33600	5·05412

The Heilbür spring is situated in the valley of Wehr, being 255 meters above the surface of the North Sea. 1,000 parts of the water contain 3·5924 parts of solids containing 5·19 parts of $FeCO_3$. Its temperature is 8·25° R.

The Sauerbrunnen at Bell is distinguished by its richness in organic substances. The Sauerbrunnen at Mühlbach near Rieden has a constant temperature of 6·5° R., and is situated 362 meters above the North Sea. 1,000 parts contain 3·33 parts of solids.

The Sulzbrunnen lies 288 meters above the sea level and has a temperature of 7° R.

The Erlenborn spring in the valley of Obermendig is situated 295 meters above the North Sea, and has a temperature of 9° R. It contains the largest quantity of calcium and magnesium carbonates of all the springs of Lake Laach. 10,000 parts contain 1·145 parts of $FeCO_3$.

The Punterbrunnen near Kell has a temperature of 8·5° R., and lies 184 meters high.

The Fehlenborn in the Brohl valley has a temperature of 11·4° R., and contains 2·317 parts of solids in 1,000 parts of water.

In conclusion, the author mentions the remarkable circumstance that, although various springs existed in this valley in former times, the supplies of which are now exhausted, they seem to have been entirely free from carbonate of iron, or at least very poor in this constituent—a fact which is very rarely observed at the present time.

D. B.

Organic Chemistry.

Action of Hydrochloric Acid on the Olefines. By J. A. Le Bel (*Compt. rend.*, lxxxv, 852—854).—From the action of hydrochloric acid on the butylenes, amylenes and hexylenes, the author has deduced the following law:—"The olefines of the constitution $CH_2=CRR'$, and $CHR=CR'R''$, in which R,R', and R'', are different or the same alcohol-radicles, combine with hydrochloric acid in the cold, whereas those of the constitution $CH_2=CHR$, and probably $CHR = CHR'$, are not attacked thereby."

This law requires to be verified by further examples.

L. T. O'S.

Butylene and its Derivatives. By E. PUCHOT (*Compt. rend.*, lxxxv, 757—760).—Butylene [iso-] is prepared by the action of 100 parts of sulphuric acid on 100 parts of butyl alcohol in presence of a mixture of 40 parts of potassium sulphate and 160 parts of calcium sulphate. It is a gas which condenses at – 40° to a liquid, and resembles ethylene in all its properties.

By the action of chlorine on butylene, first a homologue of ethylene dichloride is obtained, viz., butylene dichloride, $C_4H_8Cl_2$, in which, by the further action of chlorine in direct sunshine, two molecules of hydrogen are replaced, yielding a body having the composition $C_4H_4Cl_6$; and if the action be further continued in sunshine and over a fire, this last body loses one molecule of hydrogen, which is not replaced by chlorine, the product having the composition $C_4H_2Cl_6$.

By the action of potash, the first body lost more than 1 molecule of hydrochloric acid, and the author thinks it probable that by continually treating it with fresh quantities of potash, 2 mol. HCl might be removed, leaving a chloride of carbon, C_4Cl_6.

The compound $C_4H_4Cl_6$, twice treated with potash, loses 4HCl, leaving C_4Cl_2; and $C_4H_2Cl_6$, which is much more easily attacked by alcoholic potash, also loses 2HCl, and is converted into C_4Cl_4.

L. T. O'S.

Liquefaction of Acetylene. By CAILLETET (*Compt. rend.*, lxxxv, 851—852).—By subjecting acetylene at 18° to a pressure of 83 atmospheres, it is condensed to a colourless, mobile, refractive liquid, lighter than water, in which it is soluble. It dissolves paraffin and many fats.

The relation which exists between the tensions of the vapours of acetylene, ethylene and ethane, is as 1 : 2 : 3.

Ethane at a temperature of 4° liquefies under a pressure of 46 atmospheres. L. T. O'S.

Valerylenes from Isobutylcarbinol. By FLAVITSKY and KRILOFF (*Bull. Soc. Chim.* [2], xxviii, 347—348).—By the action of alcoholic potash on amylene bromide (b.-p. 25°), a valerylene is obtained boiling at 28—30°, and forming compounds with copper and silver. The latter has the composition C_5H_7Ag. The product yielded by this hydrocarbon on oxidation, together with its mode of formation, lead the authors to regard it as isopropylacetylene.

The bromide of trimethylethylene, treated in the same way, yields amylene monobromide, and a small quantity of a volatile hydrocarbon, which exhibits no tendency to form compounds with copper and silver. This valerylene boils at 34°.

These researches are not yet complete. C. F. C.

Formation of Ethers, at Low Temperatures, by means of Hydrochloric Acid. By E. DEMOLE (*Deut. Chem. Ges. Ber.*, x, 1790—1791).—The author has extended the observation of Friedel, relating to the formation of ethers by the action of hydrochloric acid upon a mixture of an organic acid with phosphoric anhydride, in presence of an alcohol, at temperatures from 80° to 200°, to temperatures relatively low. At 0° this reaction between acetic acid and ethyl alcohol is complete: so also with amyl alcohol. The author finds, further, that by the action of dry hydrochloric acid gas upon a mixture of glacial acetic acid and phosphoric anhydride at 0°, acetyl chloride is formed. This is direct evidence in favour of Friedel's view of the production of ethers by the above reaction being due to the formation of a chloranhydride, which decomposes the alcohol to form a mixed ether.

C. F. C.

Boric Ethers. By CONST. COUNCLER (*Deut. Chem. Ges. Ber.*, x, 1655—1657).—Allyl borate combines directly with 6 atoms of bromine. The *hexbromide* is obtained by gradually mixing solutions of the two substances in carbon bisulphide, distilling off excess of bromine and bisulphide, and passing dry carbon dioxide over the residue. It is a thick brownish liquid decomposing below its boiling-point; non-inflammable; colours feebly luminous flames an intense green. Its composition agrees with the formula $(C_3H_5Br_2O)_3B$. When left in contact with water, it is resolved into boric acid and dibromopropyl alcohol, a body which Markownikoff obtained by direct addition of bromine to allyl alcohol.

Allyl borate reacts with zinc ethide to form a colourless highly refractive liquid, boiling at 110—120°, the composition of which is not yet made out.

Boric anhydride reacts with isobutyl alcohol, when the two are heated to 160—170° in sealed tubes, to form isobutyl borate, $(C_4H_9O)_3B$, a colourless mobile liquid, burning with a green flame, boiling at 212°, and gradually decomposing in contact with water.

Boron trichloride, acting on benzyl alcohol, forms dibenzyl.

J. R.

Action of Certain Oxides on the Chlorhydrin of Ethylene Glycol. By M. KASCHIRSKY (*Bull. Soc. Chim.* [2], xxviii, 350).—The author infers from many known reactions the possibility of converting the oxides of the olefines into the corresponding isomeric aldehydes. By the action of the oxides of zinc and lead upon ethylene chlorhydrin, acetic aldehyde is formed and not ethylene oxide, as is the case with the alkalis. To determine the influence of temperature upon the formation of the one or other of these isomerides, the author has subjected the chlorhydrin to the action of potash at 160—180.°

Ethylene oxide is the product of the reaction. C. F. C.

Solubility of Sugar in Water. By H. COURTONNE (*Compt. rend.*, lxxxv, 959—961).—The author confirms the results of Berthelot and Scheibler that—

At 12·5° 100 grams of water dissolve 198·647 grams of sugar.
„ 45° „ „ 245 „

Or—

A saturated solution at 12·5° contains 66·5 per cent. of sugar.
„ 45° „ 71 „ „

L. T. O'S.

Influence of the Alkalinity of Different Substances on the Rotatory-power of Sugar. By H. PELLET (*Bull. Soc. Chim.* [2], xxvii, 250).—The author demonstrates that there is no relation between the action of alkalis on the rotatory power of sugar and their equivalents; the same is true for different bodies having alkaline reaction.
P. P. B.

Iodide of Starch. By L. BONDONNEAU (*Compt. rend.*, 671—673). —When excess of iodine is added to a solution of starch, iodide of starch separates out as a blackish-violet substance, which, when washed and dried, exhibits a coppery lustre. When heated to 100° it loses 16—18 per cent. of hydriodic acid and water, and at 190° the loss amounts to 46 per cent., and the colour changes to black. This black substance yields on oxidation saccharic and oxalic acids; sulphuric acid converts it into glucose. When the iodide is heated under pressure carbon dioxide, hydriodic acid, and iodine are evolved, and when heated to 100° with water under pressure, it partly dissociates into iodine and starch, and partly decomposes into glucose and hydriodic acid. Water at the ordinary temperature slowly decomposes it into α-dextrin and hydriodic acid. It is decomposed by diastase into glucose, β- and γ-dextrin, hydriodic acid, and an organic iodide not yet separated. Its taste is insipid. The different analyses give results from which the formula $(C_6H_{10}O_5)_5I$ is deduced.
L. T. O'S.

Chloral Hydrate. By C. O. CECH (*Wien. Akad. Ber.*, lxxv, 299—312). This paper, containing an account of chloral anilide, chlorotoluide, &c., and of the derivatives of chloral cyanide-cyanate has already appeared in this *Journal* (1876, i, 376; ii, 184; 1877, i, 67). The grounds for regarding chloral cyanide-cyanate as a molecular compound of hydrocyanic acid and cyanic acid with chloral, and not as a trichlorinated lactylurea, are the following:—This compound is formed by the direct union of chloral-cyanide with cyanic acid. It is decomposed by solution in cold aniline, hydrocyanic acid being given off, and the cyanic acid splitting up into carbon dioxide and ammonia. Chloral-anilide obtained by the action of aniline on chloral cyanide-cyanate is identical with the anilide prepared directly from chloral hydrate. This shows that the chloral molecule remains intact:—

$$\underset{\text{Chloral cyanide cyanate.}}{C_4H_3Cl_3N_2O_2} + C_6H_7N + H_2O = \underset{\text{Chloral anilide.}}{C_8H_7Cl_2NO} + HCN + CO_2 + NH_4Cl$$

$$\underset{\text{Chloral.}}{C_2Cl_3HO} + C_6H_7N + CNK = C_8H_7Cl_2NO + HCN + KCl.$$

W. C. W.

Ammonia Derivatives of Chloral. By R. SCHIFF and G. TASSINARI (*Deut. Chem. Ges. Ber.*, x, 1783—1787).—The objects of this investigation are to determine,—1. Whether the property of uniting with the amides of the fatty and aromatic acids is common to all chlorals and bromals. 2. Whether the addition-products thus obtained are in all cases identical with the compounds obtained by replacing a hydrogen-atom of the amide group in the chloral-ammonias by the corresponding acid radicle; and 3. The mode of action of the aldehydes upon the chloral-ammonias. The authors establish the identity of the product of the reaction of acetic anhydride upon butyl-chloral-ammonia with that of acetamide upon butyl-chloral; in each case acetyl-butyl-chloral-ammonia—

$$CCl_3.(CH_2)_2.CH.(OH).NH.C_2H_3O$$

is formed. By the action of benzamide upon butyl chloral, benzoyl-butyl-chloral-ammonia, $CCl_3.(CH_2)_2CH(OH)NH.CO.C_6H_5$ is formed. It is insoluble in water, soluble in alcohol and ether; it melts at 132—133°. The action of benzoyl chloride upon butyl-chloral-ammonia fails to yield this body in a condition fit for analysis. By the action of bromal upon acetamide, acetyl-bromal-ammonia,

$$CBr_3.CH(OH).NH.(C_2H_3O)$$

is formed. This compound is soluble in alcohol and ether; the crystals melt at 160°. These facts lead to an affirmative solution of the first two problems.

Action of the Aldehydes upon Chloral-ammonia.—With the aldehydes of the methyl series unsatisfactory results were obtained. By the action of benzaldehyde upon chloral-ammonia, however, a well-defined crystalline product is obtained, which melts at 121°, and analyses as $C_{20}H_{20}Cl_8N_6O$. The authors withhold any conclusion respecting the constitution of this and similar bodies until they are in possession of the results of a more complete investigation. C. F. C.

Acrolein Hydrochloride. By M. KRESTOWINKOFF (*Bull. Soc. Chim.* [2] xxviii, 350). The result of this investigation is to show that Geuther's acrolein hydrochloride, $C_3H_4O.ClH$, is the aldehyde of β-chloropropionic acid, this acid having been obtained by oxidizing the hydrochloride in question with nitric acid. C. F. C.

Glyoxaline. By. G. WYSS (*Deut. Chem. Ges. Ber.*, x, 1365—1375). In continuing his research (*ibid.*, ix, 1543) on glyoxaline, $C_3H_4N_2$, and glycosine, $C_6H_6N_4$, the bases which Debus obtained by acting with ammonia on glyoxal, the author has found Lubawin's process for the preparation of glyoxal advantageous. Into glass cylinders, each of ¼ liter capacity, are poured, by means of a funnel tube, and without mixing, separate portions of 160 c.c. 50 per cent. aldehyde, 20 c.c. of water, and 64 c.c. of nitric acid (sp. gr. 1·37) mixed with 2·5 c.c. fuming acid. The vessels are allowed to stand undisturbed. In summer the reaction is complete in four or five days, and the contents may at once be evaporated on the water-bath. The residue consists chiefly of glyoxal (according to Lubawin, from 100 grams aldehyde 45—100 grams of the compound of glyoxal with sodium bisulphite may be obtained). To prepare glyoxaline, the residue is treated very gradually with strong ammonia in slight excess, the temperature being kept down. Glycosine then separates as a brown powder, which may be filtered off. The filtrate is boiled with lime to expel ammonia, and evaporated to a syrup. This is exhausted with absolute alcohol, and the alcoholic solution fractionally distilled.

In the (Russian) paper from which the process is taken, Lubawin shows that formic acid is really generated by the action of ammonia on glyoxal, thus confirming Debus's explanation of it—

$$2C_2O_2H_2 + 2NH_3 = C_3H_4N_2 + H_2CO_2 + 2H_2O.$$

Acetyl and benzoyl chlorides and acetic anhydride are entirely without action on glyoxaline, even when heated with it, or, at least, form only addition-products. From this it might be inferred that glyoxaline is a tertiary base. But if glyoxaline be boiled for some hours with ethyl bromide, the syrup remaining after evaporation on the water-bath taken up with water, the bromine removed by freshly precipitated silver chloride, and platinic chloride added to the concentrated solution, there gradually separates a salt having the composition $[C_3H_3N_2(C_2H_5.C_2H_5Cl)]_2 + PtCl_4$. From the bromethylate, by treatment with moist silver oxide, the hydroxide may be obtained as a strongly alkaline liquid, which, when dried in a vacuum over sulphuric acid, changes to a deliquescent crystalline solid. Benzyl chloride acts on glyoxaline in a perfectly similar way. From its behaviour with these ethers, in conjunction with its indifference towards acid chlorides, it may be concluded that glyoxaline contains one $\equiv NH$ group, and one atom of nitrogen united by three affinities to carbon.

Glyoxaline is quite unaffected by chromic acid, and by reducing agents of all kinds, but potassium permanganate oxidizes it completely. Formic acid and CO_2 were the only products demonstrated.

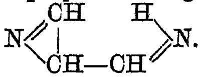
When concentrated solutions of glyoxaline sulphate and potassium nitrite, or of the hydrochloride and silver nitrite, are heated for a long time, the mixture evaporated, and the residue exhausted with absolute alcohol, a nitroso-derivative, possessed of acid properties, is obtained. The alkaline salts of this body are reddish-brown, and give with solutions of metallic salts amorphous variously-coloured precipitates.

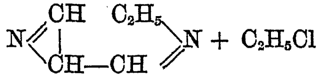
Tribromoglyoxaline, $C_3HBr_3N_2$, is produced, together with glyoxaline hydrobromide, by the action of bromine on an ethereal or (better) aqueous solution of glyoxaline. In the latter way a bright brown precipitate is formed, which may be crystallised from much boiling water. Readily soluble in alcohol, it is almost insoluble in cold water, and sparingly soluble in ether, chloroform, and carbon disulphide. It possesses the remarkable property of being soluble in alkalis, and precipitated by acids. With the exception of hydrocyanic acid, it is, in fact, the only known organic acid not containing oxygen. Most of its salts are insoluble. The silver-compound, when boiled with ethereal solutions of methyl or ethyl iodide, gives methyl and ethyl tribromoglyoxalinates, well crystallised bodies, insoluble in water and alkalis, soluble in alcohol and ether. Treated for some time in warm alcoholic solution with sodium-amalgam, the bromine in these two ethers is displaced by hydrogen, and methyl and ethyl homologues of glyoxaline are obtained, as oily soluble bases which form deliquescent hydrochlorides. Only the platinum salts were analysed.

Silver-glyoxaline is obtained as a granular insoluble precipitate when silver nitrate is added to glyoxaline solution—

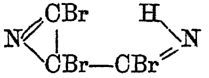
$$2C_3H_4N_2 + AgNO_3 = C_3H_3AgN_2 + C_3H_4N_2.HNO_2,$$

or better still by adding caustic soda to a mixture of glyoxaline and silver nitrate. The reaction of acetyl chloride on this body gives unsatisfactory results; methyl and ethyliodides, however, act upon it in the cold, giving, besides small quantities of the above-mentioned homologues, insoluble doughy compounds, as yet uninvestigated.

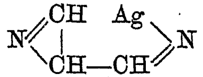
To explain the formation and properties of glyoxaline the author attributes to it the constitution . Its incapability of yielding an acetyl-derivative with acetyl chloride is no proof of the absence of an imide group, since, amongst others, the phenylated guanidines exhibit the same peculiarity. Assuming this constitution, some of the above bodies may be thus formulated:—



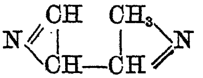
Chlorethylate of glyoxaline.



Tribromoglyoxalinic acid.



Silver glyoxaline.



Methyl glyoxaline.

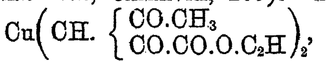
Glycosine has been as yet but little examined. Ch. B.

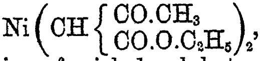
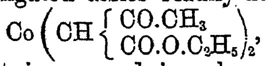
Decomposition of Hydrochloride, Hydrobromide, and Hydriodide of Trimethylamine by Heat. By C. Vincent (*Compt. rend.*, lxxxv, 666—671).—On heating trimethylamine hydrochloride to 285°, trimethylamine and methyl chloride are evolved, whilst a residue of the hydrochloride of monomethylamine and trimethylamine remains; a little above 305°, ammonia and methylchloride escape; and finally at 325° the whole decomposed.

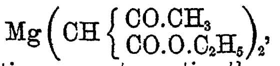
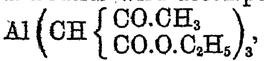
In a similar manner the hydrobromide and hydriodide of trimethylamine are decomposed, the former between 230 and 300°, and the latter between 210 and 280°.

By the above methods chloride and bromide of methyl may be prepared in large quantities; but, owing to the energetic action of iodide of methyl on trimethylamine, it is impossible to obtain large quantities of the iodide. L. T. O'S.

On Acid Acetates. By A. Villiers (*Compt. rend.*, lxxxv, 755—757).—The author admits the correctness of Lescœur's formula for sodium biacetate. He has prepared hydrated calcium biacetate, $C_2H_3CaO_4.C_2H_4O_2.H_2O$. Neutral acetates when exposed to an atmosphere saturated with acetic acid, absorb it in the same manner as anhydrous salts absorb water, to form hydrates. L. T. O'S.

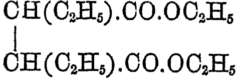
Metallo-aceto-acetic Ethers. By MAX CONRAD (*Liebig's Annalen*, clxxxviii, 269).—The *copper-aceto-acetic ether* of Geuther,  $Cu\left(CH.\left\{\begin{array}{l}CO.CH_3\\CO.CO.O.C_2H\end{array}\right.\right)_2$, is easily obtained by shaking an ammoniacal copper sulphate solution with aceto-acetic ether; it is insoluble in water, but readily soluble in hot benzene, alcohol, carbon disulphide, ethyl iodide, and bromobenzene, crystallising unchanged from these solvents. The brilliant green needles thus obtained partially sublime without alteration when carefully heated to 178°; at 182° they melt, and at higher temperatures are decomposed with production of metallic copper.

Nickel aceto-acetic ether,  $Ni\left(CH\left\{\begin{array}{l}CO.CH_3\\CO.O.C_2H_5\end{array}\right.\right)_2$, is similarly obtained by employing a solution of nickel sulphate, chloride of ammonium, and ammonia; it is soluble in hot benzene and ether, crystallising in microscopic elongated tables readily decomposed by water. *Cobalt aceto-acetic ether*,  $Co\left(CH\left\{\begin{array}{l}CO.CH_3\\CO.O.C_2H_5\end{array}\right.\right)_2$, is identical in properties, excepting that it is rose-red in colour, whereas the nickel-compound is green.

Magnesium aceto-acetic ether,  $Mg\left(CH\left\{\begin{array}{l}CO.CH_3\\CO.O.C_2H_5\end{array}\right.\right)_2$, may be obtained in the same way, only acting on aceto-acetic ether with magnesium amalgam; it crystallises from hot benzene in shining plates, and melts with decomposition at 240°. *Aluminium aceto-acetic ether*,  $Al\left(CH\left\{\begin{array}{l}CO.CH_3\\CO.O.C_2H_5\end{array}\right.\right)_3$, is obtained in slender, shining needles, when potassium aluminate and aceto-acetic ether are mixed and the solution allowed to stand; it melts at 76° without decomposition, and on heating evolves brown vapours containing aluminium; by cautiously heating it can be distilled unchanged, the distillate solidifying to a crystalline mass melting at 76°. The zinc and lead compounds obtained similarly could not be crystallised, and contained excess of base; the silver compound readily decomposes, even in the dark; platinum, gold, tin, and chromium compounds could not be prepared. Freshly precipitated mercuric oxide evolves heat on treatment with aceto-acetic ether, forming a white insoluble mass.

These derivatives are quite analogous to the acetyl-dichloracetic ether formerly obtained by the author; the ready formation of these substances indicates that the hydrogen of the methylic group of acetic ether, $CH_3.CO.O.C_2H_5$, is easily replaceable both by electro-positive and electro-negative elements and radicles, when some of that hydrogen has been already displaced by a negative radicle such as acetyl; this displacement, consequently, is possible only with the α-acetylated compound ethers; thus, the β-acetylated propionic ether of the author (in which the acetyl is not in union with the carbon-atom already connected with the $CO.O.C_2H_5$ group) does *not* give rise to such derivatives, nor could Hellon and Oppenheim form a mercury-compound of propionyl-propionic ether. C. R. A. W.

Ethylic Ethylmethylaceto-acetate, Ethylmethyl-acetic Acid, and α-Ethylmethyl-β-Oxybutyric Acid. By RICHARD SAUR (*Liebig's Annalen*, clxxxviii, 257).—Erlenmeyer and Hell did not succeed in preparing ethylmethyl acetic acid, $CH(CH_3)(C_2H_5).COOH$, synthetically, by the action of metallic silver on a mixture of methyl iodide and bromobutyric ether, $CHBr(C_2H_5)—CO.OC_2H_5$ (from the action of bromine on fermentation butyric acid), as this reaction gave rise only to an inflammable gas (ethane?) and ethyl suberate,

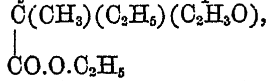


$$\begin{array}{l}CH(C_2H_5).CO.OC_2H_5\\ |\\ CH(C_2H_5).CO.OC_2H_5\end{array}$$

; but as the other four theoretically possible valeric acids are all different from optically active valeric acid, they considered this latter to be ethylmethyl-acetic acid.

To test the correctness of this deduction, the author has prepared ethylmethyl-acetic acid from ethylic sodethyl-aceto-acetate, and methyl iodide, and comparing it with other valeric acids: in boiling point and other properties, and notably in the formation of an uncrystallisable barium salt, it agrees absolutely with the active valeric acid; but as far as minute amounts of material enable him to decide, the author finds that it has no action on polarised light: this point, however, is under further examination.

Ethylic ethylaceto-acetate boiling between 192 and 196° was diluted with about its own volume of pure benzene, and then treated with sodium so as to form *ethylic sodethylaceto-acetate*, which was then decomposed by the equivalent quantity of methyl iodide. After purification, the ethylic *ethylmethylaceto-acetate*,



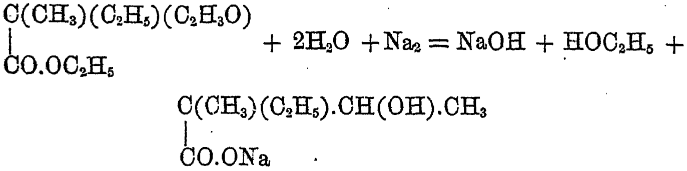
$$\begin{array}{l}C(CH_3)(C_2H_5)(C_2H_3O),\\ |\\ CO.O.C_2H_5\end{array}$$

obtained, boiled at 198° (not corrected), and had the sp. gr. 0·974 at 22°, compared with water at 17·5°; it is not miscible with water, but readily mixes with alcohol, ether, and benzene; sodium does not act on it, and ferric chloride colours it violet.

In distilling it with sodium ethylate (freed from excess of alcohol by heating to 200° in a stream of hydrogen), acetic ether and alcohol are formed in quantity greater in proportion to the amount of the ether compared with the sodium ethylate; equal numbers of molecules give very little, but when the ratio is 4 molecules to 1, considerable amounts are formed. Besides these, *ethylmethyl acetate of ethyl*, $CH(C_2H_5)(CH_3)—CO.OC_2H_5$, is formed, boiling at 132—133°, and of sp. gr. 0·8695 at 22°, compared with water at 17·5°; it is not soluble in water, but is miscible in all proportions with alcohol, ether, and benzene.

Alcoholic potash saponifies this ether, forming potassium methylacetate, obtainable as a highly-deliquescent crystalline crust by passing carbon dioxide into the fluid, evaporating to dryness, extracting with absolute alcohol, and evaporating in a vacuum. By distillation with dilute sulphuric acid, *ethylmethyl-acetic acid* itself was obtained, boiling at 173° (not corrected) and of sp. gr. 0·938 at 24°, compared with water at 17·5°, it seems to retain water energetically, probably as the hydrate $C_4H_9.C(OH)_3$: in water it is sensibly, but not very soluble. The silver-salt forms feathery needles when crystallised from boiling water; these are scarcely affected by light; the calcium salt is a crystalline mass of anhydrous needles, but the barium salt *exhibits no trace of crystallisation*, its solutions always drying up to varnishes: on comparing this salt with barium isovalerate (from isobutyl cyanide), the latter crystallised in long prisms to the last drop.

When ethylic ethylmethyl-aceto-acetic is treated with water and sodium-amalgam, it becomes hydrogenised and saponified, forming the sodium salt of *α-ethylmethyl β-oxybutyric acid*, thus:—



$$\begin{array}{l}\mathrm{C(CH_3)(C_2H_5)(C_2H_3O)}\\ |\\ \mathrm{CO.OC_2H_5}\end{array} + \mathrm{2H_2O} + \mathrm{Na_2} = \mathrm{NaOH} + \mathrm{HOC_2H_5} + \begin{array}{l}\mathrm{C(CH_3)(C_2H_5).CH(OH).CH_3}\\ |\\ \mathrm{CO.ONa}\end{array}$$

The sodium salt is obtained pure by neutralising with sulphuric acid, evaporating to dryness, extracting with absolute alcohol, again evaporating to dryness, and washing the residue with *very little* absolute alcohol; crystalline nearly white nodules are thus left undissolved. From this the silver salt was prepared, readily soluble in hot and moderately soluble in cold water, and containing $C_7H_{13}AgO_3$: the copper-salt is basic, being $C_7H_{12}CuO_3$. The free acid was obtained from the sodium salt by decomposing with hydrochloric acid and treating with ether; it is readily soluble in water, less so in saline solutions; over sulphuric acid it becomes first viscid and then solid, probably with formation of an anhydro-derivative.

C. R. A. W.

Salts of Tetracrylic and Diaterpenylic Acids. By OTTO KRAFT (*Deut. Chem. Ges. Ber.*, x, 1659—1661).—Tetracrylic acid is converted, by prolonged heating of its sodium-salt with potash-ley, into an isomeric acid, of which the calcium salt, $(C_7H_{11}O_2)_2Ca$, is more soluble in cold than in hot water.

The salts of diaterpenylic acid are perfectly stable. The *barium salt*, $C_8H_{12}BaO_5$, H_2O, formed by neutralising the acid with barium hydrate, crystallises in groups of needles on evaporating its solution over sulphuric acid. It is deposited from its aqueous solution on heating. The *silver salt*, $C_8H_{12}Ag_2O_5$, is thrown down as a curdy precipitate on adding silver nitrate to the barium salt. The *ethylic ether* obtained by heating the silver salt with ethyl iodide is solid at common temperatures, and has a peculiar odour when warmed.

J. R.

Decomposition of Brassic Acid by Caustic Potash. By G. GOLDSCHMIEDT (*Wien. Akad. Ber.*, lxxiv, 394—398).—Meyer has shown that oleic acid and its isomeride, elaidic acid, both yield acetic and palmitic acids on fusion with caustic potash (*Ann. Chem. Pharm.*, xxxv, 174). In the same way, erucic and brassic acids are decomposed by fusion with caustic potash into acetic and arachidic acids.

These isomeric acids may be represented by the following formulæ:—

Oleic and elaidic acids.

$$H_{32}C_{16}{=}CH{-}CO_2H \qquad H_4C_2{=}C_{15}H_{29}{-}CO_2H$$

Erucic and brassic acids.

$$H_{40}C_{20}{=}CH{-}CO_2H \qquad H_4C_2{=}C_{19}H_{37}{-}CO_2H.$$

W. C. W.

Distillation-products of Xanthates (Ethyl Dithiocarbonates). By A. FLEISCHER (*Deut. Chem. Ges. Ber.*, x, 1293).—According to Zeise, the so-called *thial ether*, $C_2H_{12}SO_3$, results (with other substances) when xanthates are submitted to dry distillation; Couerbe found xanthin gas, COSH; xanthil, $C_4H_{10}O_3$; and xanthurin, $C_8H_{16}SO_4$; whilst Sacc obtained none of these, but instead, carbonic acid, sulphuretted hydrogen, mercaptan, carbon disulphide, &c. The author and W. Hanke find that sodium and potassium xanthates yield the same distillation-products, from which carbon sulphide, the mono- and disulphides of ethyl, and carbon oxysulphide gas were separated when anhydrous salts were used; and mercaptan, carbon disulphide, alcohol, the two ethyl sulphides, and carbonic acid and sulphuretted hydrogen gases, when salts containing water of crystallisation were employed. Lead xanthate furnishes the same products as the anhydrous alkaline xanthates. The ethyl sulphides in these experiments were isolated, and determined by means of their boiling points, by elementary analysis, and vapour-density estimation, and by their mercuro-chlorides and platino-chlorides. In all these respects they corresponded with the data hitherto published, but they differed in odour, possessing a more or less pleasant ethereal smell; the garlic-like odour hitherto ascribed to them is, therefore, doubtless due to impurity. The carbon oxysulphide was distinguished by forming no precipitate in acid silver solutions, but a black one with ammoniacal silver; by producing carbonate and sulphide of barium with baryta-water; and by forming with alcoholic potash a crystalline mass of ethylmonothiocarbonate of potassium, $K.C_2H_5.CO_2S$. Probably the xanthurin of Couerbe was simply a mixture of the two ethyl sulphides, and his xanthin gas an impure carbon oxysulphide containing sulphuretted hydrogen and mercaptan vapour; the discovery of carbon oxysulphide, therefore, belongs of right to Couerbe (1840), although he did not isolate it in a pure state; since then and up to 1867, however, carbon oxysulphide was always regarded as simply a mixture of carbonic acid and sulphuretted hydrogen. C. R. A. W.

Dipropyloxalic Acid. By M. WORONTSOFF (*Bull. Soc. Chim.* [2], xxviii, 350).—The author has prepared dipropyloxalic acid $C.(C_3H_7)_2.OH.COOH$, and is engaged in investigating its reactions.

C. F. C.

The Action of Bromine on Pyrotartaric Acid. By EDMD. BURGOIN (*Ann. Chim. Phys.* [5], xii, 419—429).—The action of bromine on pyrotartaric acid varies with the relative proportions of bromine and acid.

If equal numbers of molecules of bromine and pyrotartaric acid are heated to 120° in presence of water, the products consist (1) of a few drops of an oily liquid, which appears to be monobromopyrotartaric acid, but has not been obtained in sufficient quantity to yield trustworthy results; and (2) bromocitrapyrotartaric anhydride, which is deposited in crystals from the solution. From this it appears that the monobrominated derivatives of pyrotartaric acid are more readily acted on than the acid itself.

When two molecules of bromine act on one molecule of pyrotartaric acid, bromocitrapyrotartaric anhydride is alone formed, and not, as Lagermark states (*Zeit. für Chem.*, vi, 299), bromoform, oxybromoform, bromocitraconic anhydride, &c., with the last of which bodies, bromocitrapyrotartaric anhydride is isomeric; its formula is therefore $C_5H_3BrO_3$. Its formation is explained as follows:—First, an unstable dibromoderivative is formed: $C_5H_8O_4 + 2Br_2 = C_5H_6Br_2O_4 + 2HBr$, which loses one molecule of hydrobromic acid and water, forming bromocitrapyrotartaric anhydride, $C_5H_6Br_2O_4 = C_5H_3BrO_3 + HBr + H_2O$. When heated with water under pressure, it decomposes into carbon dioxide and water.

By the action of four molecules of bromine on pyrotartaric acid, allylene tetrabromide, or some isomeric body, should be formed, but hydrobromide of ethylene tribromide, an isomeride of acetylene tetrabromide, is actually obtained, carbon dioxide and water being at the same time evolved. It is a liquid solidifying at −17°.

L. T. O'S.

Normal Pyrotartaric Anhydride. By V. MARKOWINKOFF (*Bull. Soc. Chim.* [2], xxviii, 349—350).—The author details the results of his researches on the formation of this anhydride, the object of which is to ascertain the relation, if any exists, between the position of the carboxyl group in isomeric acids, and the constitution of their respective anhydrides.

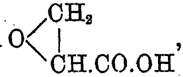
The results obtained in the endeavour to prepare the anhydride by the dry distillation of normal pyrotartaric acid, both alone and together with phosphoric anhydride, proving unsatisfactory, the author avails himself of the action of acetyl chloride, in ethereal solution, upon the silver salt of the acid. The pure anhydride thus prepared crystallises in small colourless needles, which are soluble to some extent in cold, more readily in boiling ether; they are easily soluble in boiling alcohol and in glacial acetic acid; soluble with difficulty in cold water, which slowly converts them into the acid. The pure substance melts at 56—57°, and boils with partial decomposition at 282—285°. Pyrotartaric anhydride presents, therefore, considerable analogy to succinic anhydride.

C. F. C.

Ethenyltricarbonic Acid. By M. ORLOVSKY (*Bull. Soc. Chim.* [2], xxviii, 348—349).—The author has prepared the acid, $C_2H_3.(COOH)_3$, homologous with and intermediate between *methenyl*-tricarbonic acid, $CH.(COOH)_3$, prepared by Pfankuch, and *allyltricarbonic* acid, $C_3H_5.(COOH)_3$, which Simpson prepared by converting monobromosuccinic acid into the corresponding cyanide, and decomposing the latter with potash, thus:—

$$C_2H_3(CN).(COOH)_2 + 3KOH = NH_3 + H_2O + C_2H_3(COOK)_3.$$

As secondary products of the action of bromine on succinic acid, in the preparation of the monobrominated acid, a compound of the formula, $C_2H_4Br_5$, melting at 51°, and the bromides, $C_2H_2Br_2$ and $C_2H_2Br_4$, are obtained. The author hopes to obtain this acid from the bromide $C_2H_3Br_3$, through the corresponding cyanide; and further, by replacing the bromine-atoms in the same compound by hydroxyl, to obtain a new triatomic alcohol, the next lower homologue of glycerin. He has found, in effect, that by the action of silver cyanide upon this bromide, a compound of the formula, $C_2H_3.(CN)_3.3Ag(CN)$, is formed, crystallising in pearly scales. These dissolve easily in both alcohol and ether, with separation of silver cyanide, to a dense liquid, from which a crystalline body is deposited, which fuses at 42°, and is probably the tricyanide $C_2H_3.(CN)_3$. C. F. C.

Pyruvic Acid. By CARL BÖTTINGER (*Liebig's Annalen*, clxxxviii, 293—352).—The author gives a historical sketch of the results obtained by Berzelius, Völckel, Moldenhauer, Finckh, Kolbe, Kekulé, Wislicenus, Debus, Wichelhaus, Baeyer, Fittig, Klimenko, Beckurts and Otto, Grimaux, and others, as to the formation and constitution of pyruvic acid, from which it results that either of the two formulæ, $CH_3.CO.CO.OH$, or  $O\left\langle\begin{array}{l}CH_2\\ \mid\\ CH.CO.OH\end{array}\right.$, will express the relationships of this body, whilst the formula, $COH.CH_2.CO.OH$, is not well applicable, the ketonic formula first mentioned being the more probable.

In order to see whether pyruvic acid behaves like other ketonic acids on oxidation with chromic acid, forming carbonic and acetic acids, the experiment was tried with the result of obtaining these products, and nothing else (oxidation with nitric acid forms oxalic acid, as previously stated by Völckel). According to Wichelhaus, ketonic acids should first split up into *two* acids, *e.g.*,

$$CH_3.CO.CO.OH + H.OH = CH_3.CO.OH + H.CO.OH.$$

No formic acid, however, was found by the author.

Condensation of Pyruvic Acid.—On standing for some time, pyruvic acid thickens, and becomes viscid, and then furnishes by distillation more decomposition-products of higher carbon percentage, and less acetic acid than the same quantity of freshly prepared acid; the author attributes this change to the doubling of the molecule rather than to any splitting up or decomposition. On heating it alone with a reflux condenser to 170°, carbon dioxide was evolved, and a resinous mass formed, from which water dissolved out small quantities of acetic, uvic, and pyrotartaric acids. On heating a neutral solution of the barium salt to boiling, with a reflux condenser attached, for three days, carbon dioxide is evolved, and uvic, uvitic, acetic, pyrotartaric, and oxalic acids are formed to an amount jointly equal to some 7 to 10 per cent., a syrupy mass not further examined constituting the great majority of the product. By heating with hydrochloric acid on the water-bath, carbon dioxide is eliminated, and a mixture of crystallisable acids formed, one of which is difficultly soluble, melts at 201—203°, and appears to be *mesaconic acid;* the other is more easily soluble, melts at 113°, and is apparently *pyrotartaric acid.* A substance formerly obtained by the author yielded a barium salt, agreeing with that of citraconic acid, and as mesaconic acid is derivable from citraconic acid, he concludes that citraconic acid is obtainable from pyruvic acid by condensation, &c.

In order to compare the pyrotartaric acids formed from citraconic, mesaconic, and itaconic acids, the author prepared them by acting on the respective acids with zinc and alcohol, to which a few drops of hydrochloric acid were added from time to time. The three pyrotartaric acids thus obtained melted at the same temperature, 112·5°, and yielded calcium salts containing about 17·4 per cent. of water of crystallisation, and 23·4 of calcium in the dry salt, in each instance; by the action of phosphorus pentachloride, water was abstracted, and an oil formed, apparently Markownikoff's *pyrotartaric anhydride.*

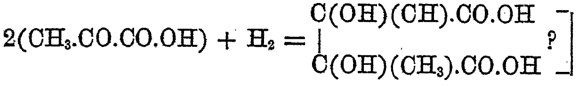
The body described as *uvitonic acid* is regarded by the author as partially decomposed dipyruvic acid; no concordant analytical numbers could be obtained, with specimens of different preparations.

Beckurts and Otto have stated that both tartaric acid and glyceric acid, when distilled, form pyruvic acid; the author could not obtain glyceric acid by heating tartaric acid with excess of baryta; but both tartaric and glyceric acids form pyruvic and also pyrotartaric acid on heating, wherefore the connections indicated by the formulæ,

$$CO(OH)—CH(OH)—CH(OH)—CO(OH)$$
$$\text{and } H—CH(OH)—CH(OH)—CO(OH),$$

are probably justifiable, notwithstanding that the latter acid cannot be obtained from the former by loss of CO_2.

Nascent hydrogen, from zinc-dust, converts pyruvic acid into lactic acid, according to Wislicenus and Debus. The author finds that in addition a new acid is formed, easily separable from the lactic acid, its zinc salt being insoluble, or nearly so; by decomposing this with sulphuretted hydrogen, a syrupy acid is obtained to the amount of some 4 to 6 per cent. of the pyruvic acid employed; this is a bibasic acid, forming two anhydrous potassium salts, $C_6H_9KO_6$, and $C_6H_8K_2O_6$, and a barium salt, $C_6H_8BaO_6 3\frac{1}{2} H_2O$. This acid he terms *dimethyltartaric acid.* [Qy. formed thus:—



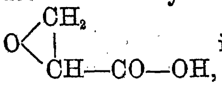
$$2(CH_3.CO.CO.OH) + H_2 = \left.\begin{array}{l} C(OH)(CH).CO.OH \\ | \\ C(OH)(CH_3).CO.OH \end{array}\right. ? \Bigg]$$

It is not volatile; the magnesium salt is readily soluble; the neutral potassium salt is precipitated by mercuric chloride and by copper sulphate, the precipitate in the latter case being readily soluble in dilute acids and ammonia, sparingly soluble in water.

When an aqueous solution of silver pyruvate is treated with *sulphuretted hydrogen,* and the liquid concentrated, acetic acid is given off, and a syrupy body formed, which can be crystallised from hot dilute sulphuric acid in needles, melting at 141°, and containing $CH_3—CH(SH)—CO.OH$, whence the author terms it *thiolactic acid* (Schwefelmilchsäure); by oxidation this body forms acetic and sulphuric acids. When heated with dilute sulphuric acid, it does not split up into thioaldehyde and formic acid, as might have been anticipated from the behaviour of lactic acid. By passing sulphuretted hydrogen through freshly prepared pyruvic acid, a white powder is separated, melting at 87°, and containing $C_6H_8SO_5$, or the elements of pyruvic acid + thiopyruvic acid, $C_3H_4O_3 + C_3H_4SO_2$. By heating this with hydriodic acid, iodine separates, thiolactic acid is formed, and a nonsulphurised body, apparently pyruvic acid; continued action of sulphuretted hydrogen also forms thiolactic acid.

A mixture of *hydrocyanic acid* and pyruvic acid is converted into lactic acid on dropping in hydrochloric acid and warming, no crystallisable acid being formed. *Ammonia gas* passed into pyruvic acid causes the evolution of carbon dioxide and formation of an oily body; aqueous ammonia forms an acid, the calcium salt of which contains 20·45 per cent. of Ca; alcoholic ammonia forms a chalky, nitrogenous substance, containing $n(C_4H_6NO_2)$, and soluble in acids and alkalis. The author regards it as the ammonia-salt of an amido-acid, which he terms *uvitonic acid*, $C_8H_9NO_4$, different from the body formerly described as uvitonic acid (this *Journal*, 1876, i, 566). This acid is readily obtained from the chalky substance by dissolving in ammonia, and adding hydrochloric acid, whereby a crystalline precipitate of the acid is thrown down. The barium salt is $C_8H_7BaNO_4.3H_2O$, of which only two-thirds are lost at 160°; it crystallises in small needles. The calcium salt crystallises in hard, transparent nodules, and in white coherent needles, containing $C_8H_9CaNO_5.5H_2O$, and $C_8H_9CaNO_5,2H_2O$, respectively, whilst the silver salt is $C_8H_9Ag_2NO_5$; whence it appears that the body regarded as the acid, $C_8H_9NO_4$, is really an anhydride, the barium salt being properly represented as $C_8H_9BaNO_5.2H_2O$. Strong nitric acid has no action on uvitonic acid; chromic acid oxidises it to carbonic and acetic acids, and ammonia with a little of a red powder not yet investigated. By fusion with potash an acid is formed, apparently *oxyterephthalic acid*, together with pyruvic and acetic acids. When treated with an ethereal solution of aniline, pyruvic acid evolves heat, and forms an anilide, $C_3H_4O_3 + C_6N_5.NH_2 = H_2O + C_9H_9NO_2$. This darkens at 114°, and melts at 122° with decomposition; it forms a barium salt, $(C_9H_8NO_2)_2Ba$. On fusion with potash, it seems to undergo an isomeric change, forming a strong acid of the same composition, sublimable in needles, which turn brown at 220°, and decompose at 240°, and forming a barium salt, $(C_9H_8NO_2)_2Ba$, after drying at 130°. When added to melting anthranilic acid, an acid is formed, containing apparently $C_{10}H_9NO_4$, the barium salt being $C_{10}H_7BaNO_4$; but this has not been obtained pure.

From all these results the author concludes that whilst the constitution of pyruvic acid cannot be deduced from its origin, the breaking up of tartaric acid on heating being complex, the behaviour of pyruvic acid towards hydrogen, sulphuretted hydrogen, and hydrocyanic acid is indicative of its possessing a ketonic character; he does not, however, decide definitely which of the two formulæ, $CH_3—CO—CO.OH$, or



$$O\left\langle\begin{matrix} CH_2 \\ | \\ CH—CO—OH, \end{matrix}\right.$$

is to be preferred.

C. R. A. W.

Note on Tartronic Acid. By E. DEMOLE (*Deut. Chem. Ges. Ber.*, x, 1788—1790).—The conversion of dinitrotartaric acid into tartronic acid, by exposing its aqueous solution to a temperature of 30°, is proved by the author to take place directly, without the formation of intermediate compounds.

The formation of oxalic acid, with evolution of carbonic anhydride and nitric oxide gases, which occurs when the temperature is allowed to rise to 50°, is referred to the secondary decomposition of tartronic by nitric acid, these acids resulting from the following reactions:—

(1.) $(CH.ONO_2)_2.(CO.OH)_2 = CO_2 + N_2O_3 + CH.OH.(CO.OH)_2$ and
(2.) $H_2O + 3N_2O_3 = 2HNO_3 + 4NO$.

Guided by the above facts, the author has devised a method for converting dinitrotartaric into tartronic acid at higher temperatures, and therefore much more rapidly: the essence of which consists in eliminating the nitric acid at the instant of its formation, and thus preventing the secondary conversion into oxalic acid. 60 c.c. alcohol, sp. gr. 0·925, are heated in a porcelain dish on a water-bath, and 20 grms. of dinitrotartaric acid added in successive small portions. The heating is continued until the evolution of gas has ceased, and the solution is allowed to crystallise. The acid is purified by recrystallisation. The author has determined its melting point to be 150—151°.

C. F. C.

Pyromeconic Acid. By E. IHLÉE (*Liebig's Annalen*, clxxxviii, 31—42).—When pure dry meconic acid is gradually heated in a tube which is bent at an obtuse angle, and the sublimate is re-distilled, almost the whole comes over at 227—228°, when the mercurial column is completely immersed in the vapour. Neither oily products nor acetic acid are formed, and only at the end of the second distillation does the temperature suddenly rise, gases being evolved; and if the operation be not then stopped, a small quantity of feathery crystals, consisting probably of Stenhouse's paracomenic acid, sublimes. The yield of pyromeconic acid was 25 per cent. of the meconic acid employed. It crystallises from hot water in long, brilliant, four-sided prisms, does not dissolve freely in ether, which however on shaking it repeatedly with an aqueous solution, takes it up almost completely.

The pure acid begins to sublime at 100°, and melts at 121·5°; it is a strong acid, decomposing alkalis and forming well defined salts. An alcoholic solution of the acid and alcoholic potash form a crystalline magma, which after washing with alcohol and drying, consists of $C_5H_3O_3K$. In the light it gradually turns bluish-green, green, brown, and after some weeks becomes colourless again. It is decomposed by heating it to 130° and by boiling it with alcohol. The barium and calcium salts are obtained by heating an aqueous solution of the acid with the carbonates only until the acid reaction ceases, or by adding the corresponding chlorides to a warm, ammoniacal solution of the acid. They crystallise in glistening needles and are acid salts $(C_5H_3O_3)_2M . 2C_5H_4O_3$. The copper salt, $(C_5H_3O_3)_2Cu$, is sparingly soluble in cold water, and crystallises from hot water in green needles. An ether of pyromeconic acid could not be obtained.

All pyromeconates are decomposed by boiling them with water, and more quickly if a free alkali be present, different products being formed, the principal being formic acid and an acid forming amorphous salts. According to Stenhouse (*Liebig's Annalen*, xlix, 18) and Brown (*ibid.*, lxxxiv, 32), from a solution of the acid in an excess of potash, the free acid separates; in this case probably decomposition had taken place and sufficient formic acid was formed to neutralise not only the potash, but also to precipitate some of the undecomposed acid. Comenic acid is also decomposed by boiling it with baryta-water, but more slowly, with apparently the formation of the same products.

C. S.

Action of Ferricyanides on Metallic Silver. By J. M. EDER (*J. pr. Chem.* [2], xvi, 211—218).—The author has shown that silver acts on potassium ferricyanide, producing the ferrocyanides of silver and potassium (*Chem. Centr.*, 1876, 569); and it was supposed that the action of silver on lead ferricyanide would be analogous. Wartha (*Photograph. Correspondenz*, xiv, 154) has found that this reaction is attended with the formation of yellow silver ferricyanide, according to the equation—

$$4Pb_3Fe_2Cy_{12} + 6Ag = 6Pb_2FeCy_6 + Ag_6Fe_2Cy_{12}.$$

The author finds that the yellow precipitate formed by the action of silver on lead ferricyanide becomes whiter the more thoroughly it is washed, assuming finally a green colour owing to decomposition of silver ferrocyanide. The weight of the thoroughly washed product agrees with the formation of ferrocyanide of silver; also, as silver ferrocyanide is decomposed by hydrochloric acid and not by dilute sulphuric acid, and the lead salt by both, the ferrocyanic acid existing as silver and lead salt may be separated, and its amount determined by titration with permanganate. The results obtained and the absence of silver ferricyanide, together with the estimation of silver and lead, agree with the author's equation, which is as follows:—

$$2Pb_3Fe_2Cy_{12} + 4Ag = 3Pb_2FeCy_6 + Ag_4FeCy_6.$$

Wartha's results depend chiefly on the presence of lead ferricyanide.

P. P. B.

Potassium Superferricyanide. By Z. H. SKRAUP (*Liebig's Annalen*, clxxxix, 368—379).—Potassium superferricyanide—

$$K—Cy_3 \equiv Fe \equiv Cy_3—K$$

s best prepared by adding 18 grams of hydrochloric acid, sp. gr. 1·196, iluted with three times its volume of water, to 50 grams of potassium erricyanide and four grams of potassium chlorate dissolved in 100 .c. of hot water. The mixture, after standing for twenty-four hours in a cool place, is filtered. The addition of alcohol to the filtrate throws down a black precipitate, from which the supernatant liquid must be rapidly decanted. The crude product is purified by dissolving in water and reprecipitating with alcohol; the pure aqueous solution evaporated to dryness in a vacuum at the ordinary temperature, leaves a brittle, amorphous, black, glassy mass, which decomposes slowly at the ordinary temperature, and rapidly at 50°. Potassium superferricyanide is a hygroscopic body insoluble in absolute alcohol; it dissolves in water, forming a neutral solution, which smells of cyanogen. This solution decomposes on boiling into ferric hydrate and ferricyanide of potassium. Caustic potash decomposes it into ferric hydrate, potassium ferro- or ferri-cyanide, and potassium cyanate. The action of sodium amalgam splits it up into ferric hydrate and potassium ferricyanide.

The solution of superferricyanide gives characteristic reactions with many of the metallic salts, *e.g.*, with basic lead acetate a dark green precipitate; with silver nitrate a dirty green precipitate changing to yellow and finally to white; with ferric salts an olive-green coloration, and with ferrous salts a bluish-green precipitate. W. C. W.

Behaviour of the Thiocyanates of Potassium and Ammonium in presence of Oxygen-acids and of some Metallic Oxides. By Schlagdenhauffen and F. Wurtz (*J. Pharm. Chim.* [4], xxvi, 235—239 and 312—319).—The substitution of sulphur for oxygen in the cyanates can be effected by means of carbon bisulphide, as in the following equation: $2NCOM + CS_2 = 2NCSM + CO_2$; but the contrary substitution cannot be so easily effected; this probably arises from the fact that the oxidising agents used could act only either when fused, or in presence of water. When they were fused, the sulphur was always oxidised to sulphuric acid, thus preventing, in most cases, the formation of cyanate; small quantities of cyanate were, however, occasionally obtained. In the second case, where the oxidising agent acts in presence of water, the cyanate, if formed, would instantly be decomposed by the water.

Potassium permanganate, in presence of free hydrochloric acid, gives rise to a more or less abundant formation of perthiocyanogen.

Chromic acid with potassium or ammonium thiocyanate, forms the corresponding chromo-thiocyanate. When a small quantity of free acid is present, chromo-thiocyanic acid is formed, together with perthiocyanogen. With much free acid, perthiocyanogen and green chromic chloride are formed. Potassium bichromate has no effect by itself; the ammonium salt produces chromium thiocyanate.

Iodic acid and *potassium iodate* (the latter incompletely) precipitate perthiocyanogen. In this reaction no free iodine is formed, as it probably acts further on the thiocyanate. Ammonium thiocyanate is acted on more readily than the potassium salt.

Potassium and ammonium thiocyanates mixed with iodine and exposed to direct sunlight, form perthiocyanogen.

Hydriodic acid, bromic acid and potassium bromate, and chloric acid all produce the same effect; the latter also produces some sulphuric acid.

Nitric acid, either concentrated or dilute, oxidises all the sulphur to sulphuric acid; the liquid at the same time acquires a rose or green colour. Nitrite of potassium does not act on thiocyanates until an acid is added, when a precipitate of perthiocyanogen is formed.

Nitric oxide produces no effect, but if nitrous fumes are passed into a solution of a thiocyanate, a blood-red colour is produced, which differs from that produced by ferric chloride in that, on evaporation on the water-bath, no coloured residue is obtained.

Selenious acid added to potassium or ammonium thiocyanate, gives a precipitate of selenium, which is mixed with perthiocyanogen if hydrochloric acid be added to the solution.

Arsenious acid in presence of hydrochloric acid gives an orange precipitate, consisting of perthiocyanogen mixed with a dark-brown arsenical compound. *Arsenic acid* gives a similar precipitate, being itself reduced to arsenious acid.

Molybdic acid in presence of free acid produces a yellow colour, which gradually changes, through orange and red, to amaranth.

Tungstic acid with hydrochloric acid, is reduced, with production of a yellow, and then a red, colour. If a large excess of hydrochloric acid is present, a fine blue colour is produced, probably due to tungsten thiocyanate.

The oxides of *mercury*, *silver*, and *copper*, when heated with potassium thiocyanate, are converted into sulphides; with the ammonium salt ammonia is liberated, and double thiocyanates are formed.

Ferric oxide heated with ammonium thiocyanate, forms ferric thiocyanate; no reaction takes place with the potassium salt with this and the following oxides.

Uranic oxide produces a double salt of a yellow colour.

Chromic oxide, when freshly prepared, produces ammonium chromothiocyanate. C. W. W.

Action of Potassic Thiocyanate on Compounds of Monochloracetic Acid. By Peter Claesson (*Deut. Chem. Ges. Ber.*, x, 1346—1354).—By the action of potassic thiocyanacetate on chloracetic ether, Heintz (*Ann. Chem. Pharm.*, cxxxvi, 22) obtained a body which he named sulphocyanacetic ether, but which was incapable of yielding salts on treatment with alkalis. Acids, however, especially hydrochloric, dissolved it readily, forming (besides other bodies) an acid which he regarded as sulphocyanacetic acid. He also found that on distilling his sulphocyanacetic ether, there remained in the retort a body of the same composition, named by him pseudosulphocyanacetic ether. By the following experiments the author has now shown that Heintz's sulphocyanacetic (thiocyanacetic) acid is identical with Volhard's (*J. pr. Chem.*, 1874, 6) thiocarbimidacetic acid, and his pseudothiocyanacetic ether a polymeric form of thiocyanacetic ether.

Such an effect of hydrochloric acid as that above mentioned appeared to the author very improbable, and on repeating Heintz's experiment, he observed that the presence of water is a condition necessary for the reaction; from which he concludes that the assimilation of water is the primary change which takes place, and that thiocarbimidacetic acid is only a secondary product.

True *thiocyanacetic acid* and its salts are prepared by dissolving crystallised monochloracetic acid in an equal weight of water, neutralising with sodic carbonate, and adding the proper quantity of potassic thiocyanate. The reaction begins immediately, and after the lapse of some time the mass becomes solid, from the separation of alkaline thiocyanacetate and chloride. From the mixture of salts, freed from mother-liquor, the former is extracted by boiling alcohol, from which it separates almost completely on cooling. The mother-liquor contains, besides thiocyanacetate, salts of thioglycollic and carbaminthioglycollic acid (*vide infra*), the two latter being secondary products due to the action of the acid on the first.

Similarly, when chloracetic ether is added to a boiling alcoholic solution of potassic thiocyanate, potassic chloride separates immediately, thiocyanacetic ether being formed.

Since free thiocyanacetic acid combines very readily with water to form carbaminthioglycollic acid, it is best extracted from solution of its sodium salt by adding sulphuric acid, and at once shaking with ether. The ethereal solution, dehydrated by calcium chloride, and evaporated over sulphuric acid, gives the acid, which is separated from the accompanying small quantity of carbaminthioglycollic acid by repeated solution in absolute ether. It is thus obtained as a colourless, odourless and uncrystallisable oil, which, on gently heating, becomes polymerised into a porcellanous mass, very difficultly soluble in boiling water. A few of its salts and ethers are described.

Thiocyanacetic ether, when heated to 120° with ethyl iodide or bromide, forms ethyl thiocyanate and iodacetic or bromacetic ether. The reaction, which is quantitative, affords an advantageous method for preparing bromacetic and iodacetic acids.

If thiocyanacetates in solution are brought in contact with salts of silver, mercury or copper, thioglycollic acid is formed: for example, $Na.O.COCH_2.S.CN + 2(Ag.O.NO_2) + 2H_2O = Ag.O.COCH_2.S.Ag + NH_3 + Na.O.NO_2 + H.O.NO_2 + CO_2$. The reaction with copper salts is characteristic, an amorphous black precipitate of cuprous thioglycollate being formed on gently heating. Alkalis also decompose salts or ethers of this acid: bromine and nitric acid oxidise its salts, producing sulphacetic acid.

Carbaminthioglycollic acid, $H.O.COCH_2.S.CONH_2$, is easily formed by adding hydrochloric acid to solution of a thiocyanacetate, and leaving the mixture to spontaneous evaporation. It crystallises in large rectangular tables or rhombic prisms, and melts at 132—134°. Boiled in aqueous solution it is quickly converted into thioglycollic acid, but when heated with concentrated hydrochloric acid it yields, in addition, *thiocarbimidacetic acid*. Alkalis convert it slowly into thioglycollic acid and ammonia: bromine oxidises it energetically to sulphacetic acid. Salts of metals which easily combine with sulphur effect its decomposition very readily into thioglycollic acid, carbonic anhydride, and ammonia.

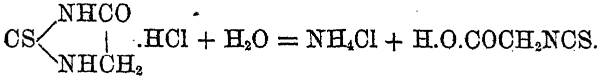
Heated to 110° with methyl alcohol and methyl iodide, carbaminthioglycollic yields *trimethyl-sulfiniodide*, which crystallises on cooling. The reaction occurs in two stages—

(1) $H.O.COCH_2.S.CONH_2 + CH_3I = H.O.COCH_2.S + CH_3.S.CONH_2$.
(2) $CH_3.S.CONH_2 + CH_3I + CH_3OH = (CH_3)_3SI + CO_2 + NH_3$.

Methyl and ethyl ethers of this acid have also been obtained by ordinary processes. The methyl ether is also obtained when methyl thiocyanacetate is heated with an equal volume of moderately dilute hydrochloric acid.

Heintz's results may now be explained. Under the influence of hydrochloric acid, thiocyanacetic ether first assimilates water to form carbaminthioglycollic ether, which is then partially decomposed into alcohol and the free acid. The latter is further acted upon, part of it absorbing water to form CO_2 and thioglycollic acid, another portion parting with water to form thio-carbimidacetic acid. Strong hydrochloric acid favours the development of the latter.

Thio-carbimidacetic acid, which the author shows to be identical with Heintz's thiocyanacetic acid, was obtained by Volhard (*loc. cit.*) by acting with chloracetic acid upon thiocarbamide; thiohydantoïn hydrochloride is thus formed, and on boiling with water splits up as follows:—



$$CS\left\langle\begin{matrix}NHCO\\ |\\ NHCH_2\end{matrix}\right..HCl + H_2O = NH_4Cl + H.O.COCH_2NCS.$$

Volhard's reaction yields the acid in theoretical quantity when chloracetic ether and thiocarbamide are boiled together for a short time in alcoholic solution. The thiohydantoïn hydrochloride crystallises out. A much better process consists in boiling together for a long time amyl thiocyanacetate and fuming hydrochloric acid, the greater part of the liberated thiocyanacetic acid passing into thiocarbimidacetic acid. The latter is colourless, easily soluble in hot, sparingly in cold water; it may be sublimed without decomposition, and melts at 125—126°. It is a feeble acid, its soluble salts being more or less decomposed by water into free acid and base.

The mercury and silver salts are insoluble. Several reactions and salts of it are described. The compounds of the heavy metals decompose it, less easily than carbaminthioglycollic acid, into thioglycollic acid, CO_2, and ammonia.

Its solution treated with silver nitrate in excess gives a crystalline compound of argentothioglycollate of ammonium.

Without doubt all these transformations have their origin in a "tendency towards neutrality" (Neutralitätsstreben), since they occur under the influence of acids or bases, or of salts of metals which have a powerful affinity for sulphur. Ch. B.

Two New Modes of Formation of Cyanamide. By DRECHSEL (*J. pr. Chem.* [2], xvi, 201—210).—I. Having observed that the carbamates of the alkaline earths are decomposed by heat, with formation of cyamides, and that there is strong evidence for regarding this as the result of the secondary decomposition of the cyanates, the author applies these facts to explain the observation of Geuther and Bilstein, who found that by the action of carbonic anhydride upon sodamide, sodium cyanamide, and not sodium cyanate, was formed. His deductions may be represented by the three equations :—

$$\text{(i.)}\ NaNH_2 + CO_2 = NH_2.CO.ONa;$$
$$\text{(ii.)}\ NH_2.CO.ONa = NCONa + H_2O;\ \text{and}$$
$$\text{(iii.)}\ NCONa + NaNH_2 = Na_2CN_2 + H_2O.$$

To prove the truth of (iii), sodamide was allowed to act upon potassium cyanate; from the product of the reaction, cyanamide in large quantity was obtained. This, taken in conjunction with the fact expressed by (ii), is undeniable evidence of the superior exactness of (i) to the equation proposed by Geuther, viz.:

$$C_2O_4 + 2NaNH_2 = C_2N_2H_2 + 2NaO + 2HO\{C = 6;\ O = 8;\ H = 1\}.$$

It is needless to add that the water formed in the above reactions decomposes a portion of the sodium amide into ammonia and sodium hydrate.

II. The decomposition of calcium carbamate by heat, with formation of cyamide, appears to occur in two steps, represented by the equations

$$\text{(i.)}\ (NH_2.CO.O)_2Ca = (N.CO)_2Ca + 2H_2O,\ \text{and}$$
$$\text{(ii.)}\ (NCO)_2Ca = CaCN_2 + CO_2.$$

To verify independently the truth of (ii), calcium cyanate (in effect a mixture of anhydrous $CaCl_2$ with $2KNCO$ was heated for some time in a platinum crucible to a low red-heat:—cyanamide was identified in large quantity in the resulting mass. Similar observations on the cyanates of barium and thallium entirely confirmed this result.

Silver cyanate exposed to a high temperature is decomposed with considerable evolution of gas, which latter, towards the end, is composed of N and CO_2 in the ratio of 10 to 22 vols. This, together with the fact that silver cyamide is entirely decomposed by heat, points to a precisely similar interpretation of the reaction which occurs, viz., $2AgCNO = Ag_2CN_2 + CO_2$. Generally, therefore, by the action of heat upon the cyanates, metallic cyamides of the form $R''CN_2$ are produced. These when treated with a small quantity of water are decomposed into monocyamides of the form $RHCN_2$; thus, *e.g.*, $2CaCN_2 + 2H_2O = CaH_2(CN_2)_2 + Ca(OH)_2$, than which, however, they are much more stable in relation to heat; thus Tl_2CN_2, $BaCN_2$ and $CaCN_2$ withstand a red heat without decomposition, whereas $NaHCN_2$ is at once decomposed on heating. In conclusion the author recommends the action of heat upon a mixture of anhydrous $CaCl_2$ with KNCO as an effective mode of preparation of cyanamide.

C. F. C.

On Amido-acids. By FRANZ HOFMEISTER (*Liebig's Annalen*, clxxxix, 6—43.)—In a recent paper, Engel (*Compt. rend.*, 80, 1168) has described two new reactions of glycine, namely, the production of a red colour with ferric chloride, and of blue on addition of phenol and a hypochlorite; these, together with its power of reducing mercurous nitrate and of preventing the precipitation of cupric sulphate by caustic soda, he considers to be characteristic of the acid. Engel himself, however, having shown (*Journ. Pharm. Chim.* [5], xxi, 194; *Chem. Centr.*, 1875, 246) that the hypochlorite reaction is exhibited by most amides, the author has systematically examined the behaviour with certain other reagents of the important group of amido-acids which are frequently met with as decomposition-products of albuminous bodies. The results may be summarised as follows:—*Glycine* and *sarcosine* give with ferric chloride red, with cupric chloride or sulphate blue, with cupric sulphate and caustic soda deep-blue solutions. They reduce mercurous nitrate, and are not precipitated by mercuric chloride, nitrate, or sulphate, or by the chloride after the addition of sodic carbonate: with the nitrate and sulphate, after such addition, they give white precipitates which are insoluble in excess of the carbonate. *Asparagine*, *aspartic acid* and *glutamic acid* give similar reactions, except that the first is precipitated by excess of mercuric chloride, and the two latter (in the cold) precipitate, as well as reduce, mercurous nitrate. These two also give with mercuric nitrate or sulphate white precipitates soluble in excess, but, after addition of sodic carbonate, precipitates which dissolve in *large* excess of the carbonate. *Leucine* behaves in general like glycine, but the precipitates with sodic carbonate and mercuric nitrate or sulphate are soluble in excess of the carbonate. *Taurine* does not react with the above-mentioned ferric, cupric, or mercuric salts alone, and does not prevent the precipitation of copper sulphate by alkalis; it reduces mercurous nitrate, and gives with sodic carbonate and mercuric nitrate or sulphate white precipitates which do not dissolve in excess of the carbonate. *Acetamide* in its reactions resembles taurine; but the precipitate with sodic carbonate and mercuric sulphate dissolves in excess of the carbonate. *Urea* also behaves in general like taurine, but gives precipitates with mercuric nitrate or sulphate, the former insoluble, the latter difficultly soluble in excess. It also precipitates mercuric chloride after addition of sodic carbonate. *Creatine* gives a red colour with ferric chloride, and blue with copper salts, and does not prevent the precipitation of copper by alkalis. It reduces mercurous nitrate. It does not precipitate mercuric salts alone, but after addition of sodic carbonate it gives with them precipitates which dissolve in excess of the carbonate, but reappear on standing. *Creatinine* differs from creatine in giving a precipitate with ferric chloride, a deep blue solution with cupric sulphate and caustic soda, and a white precipitate with mercuric chloride.

The copper salts of leucine, aspartic acid, glutamic acid and tyrosine, in consequence of their slight solubility in water, are well adapted for the detection and estimation of these acids. They may be readily prepared by gradually adding hydrated cupric oxide to boiling solutions of the acids, and filtering hot. The salts separate from the filtrate on cooling; those portions which remain with the excess of copper hydrate on the filter may be extracted with boiling water. Their exact formulæ, solubilities, and properties are given by the author. Tyrosine-copper is soluble in 1,230 parts of cold water; the other copper salts in (about) 3,000 parts.

The separation of the amido-acids is rendered difficult by the prc perty which they possess of uniting with each other to form saline compounds. A series of these compounds prepared by the author will be described in a future paper. They are all decomposed by boiling with cupric hydrate, but even so their constituents cannot be separated, since the more soluble copper salts, those of glycine and glutamic acid, for example, prevent the precipitation of the less soluble ones. Consequently the non-appearance of a crystalline precipitate on adding cupric hydrate to a boiling liquid does not prove the absence of one of the latter.

It is well known that the oxyacids and multivalent alcohols have the power of retaining in alkaline solution half an equivalent of copper for each hydroxyl-group in their molecules. Coray and Wislicenus explain this by supposing that compounds are formed in which copper takes the place of the alcoholic hydrogen. Amongst aromatic oxyacids, according to Weith (*Deut. Chem. Ges. Ber.*, ix, 342), this property is confined to those which belong to the ortho series, and is not shared by their isomerides; and Dossios (*Liebig's Annalen*, cxlvi, 174) has observed a similar difference between the isomeric lactic acids. With the exception of taurine, the above amido-acids can retain in alkaline solution a definite quantity of copper. This amount the author, by a process of titration which is fully described, has found to be, for each molecule of glycine, sarcosine, leucine, glutamic acid and tyrosine, *one-half atom* of copper, and for each molecule of aspartic acid and asparagine, *one atom* of the metal. If the compounds here formed are ordinary copper salts, it is difficult to see why they are not decomposed by alkalis. The author rather inclines to the belief that they are saline compounds in which the soda salts of the acids play the part of base, and the cupric hydrate that of acid. Evidently the solvent action on copper must be due to the presence in the amido-acid of the group $CHNH_2$, since this power is totally wanting in the fundamental acids, and their amides which contain the grouping $CONH_2$. Now cupric oxide is known to form saline compounds with ammonia and (less easily) with potash and soda; and the fact that the amido-acids are substituted ammonias, and can really play the part of bases, makes it not improbable that they can combine in a similar manner with cupric oxide, especially when their acid properties are neutralised by the presence of a great excess of alkali. Thus the compound of glycine would be $(COONa.CH.NH_2.HO)_2Cu$; that of aspartic acid $COONa.CH(NH_2.HO.CuOH).CH_2.COONa$.

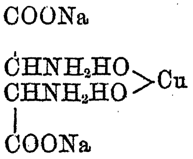
This theory does not explain why aspartic acid and its amide, asparagine, hold in alkaline solution twice as much copper as the other acids; it cannot be due to their basicity, since this increased solvent power does not appear in the bibasic glutamic acid. Ch. B.

Amido-acids. By F. HOFMEISTER (*Wien. Akad. Ber.*, lxxv, 469—498).—Leucine, tyrosine, aspartic, and glutamic acids may be isolated and detected by the insolubility of their copper salts. *Copper-leucine* $(C_6H_{12}NO_2)_2Cu$ forms pale-blue, shining, crystalline scales, soluble in 3,045 parts of cold, and in 1,460 parts of boiling water. The other copper-salts described by Goessmann (*Gmelin-Kraut*, *Supplement*, 1246), Ritthausen, and Kreussler (*Chem. Centr.*, 1871, 394) were not obtained. *Copper aspartate*, $C_4H_5CuNO_4 + 4\frac{1}{2}H_2O$, dissolves in 2,870 parts of cold, and in 234 of boiling water. It is very soluble in dilute acetic acid, and can easily be obtained in the pure state by recrystallisation from this solvent. The crystals lose their $4\frac{1}{2}$ molecules of water at 120°; the anhydrous salt is hygroscopic. *Copper glutamate*, $C_5H_7CuNO_4 + 2\frac{1}{2}H_2O$, soluble in 3,400 parts of cold water and in 400 parts of boiling water, bears a strong resemblance to the aspartate. The two other copper glutamates described by Ritthausen (*Chem. Centr.*, 1867, 276) could not be obtained.

Copper tyrosine $(C_9H_{10}NO_3)_2Cu$, forms small glistening dark-blue needles soluble in 1,230 parts of cold, and in 240 parts of boiling water, but insoluble in alcohol and ether. It is decomposed by acids, and by boiling with water.

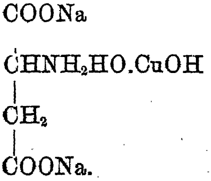
The precipitation of the four copper salts just described is hindered by the presence of free acids and by the soluble copper salts of glycine and other organic bodies. One molecule of glycine, tyrosine, sarcosine, leucine, or of glutamic acid can dissolve half an atom of copper in an alkaline solution. One molecule of aspartic acid or asparagine can hold one atom of copper in solution. The constitution of these bodies may be represented thus:—

Copper glycine.



$$\begin{array}{l}\mathrm{COONa}\\ |\\ \left.\begin{array}{l}\mathrm{CHNH_2HO}\\ \mathrm{CHNH_2HO}\end{array}\right>\mathrm{Cu}\\ |\\ \mathrm{COONa}\end{array}$$

Copper aspartate.



$$\begin{array}{l}\mathrm{COONa}\\ |\\ \mathrm{CHNH_2HO.CuOH}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{COONa.}\end{array}$$

The author also gives a tabular statement of the reactions of the amido-acids with ferric chloride, copper sulphate, mercurous and mercuric salts. W. C. W.

The Action of Bromine on Succinimide, and a New Mode of forming Fumaric Acid. By E. Kisielinski (*Wien. Akad. Ber.*, lxxiv, 561—570).—A mixture of dibromsuccinimide, monobromfumarimide and fumaric acid is obtained by heating succinimide with bromine to 130° in sealed tubes for four hours. The dibromsuccinimide is separated from the other bodies by its insolubility in water. It crystallises in slightly yellow rhombic prisms melting at 225°, soluble in warm alcohol, and slightly soluble in ether and glacial acetic acid. On evaporating the liquid from which the dibromsuccinimide has been removed, impure monobromofumarimide separates out, and fumaric acid is deposited from the mother liquor.

Monobromofumarimide dissolves readily in alcohol and in hot water; it is only slightly soluble in ether, chloroform, carbon disulphide, and glacial acetic acid. It forms faintly yellow tabular crystals, which melt at 150—152°.

The action of dry ammonia gas on a well cooled mixture of alcohol and monobromofumarimide yields transparent prismatic crystals of monobromofumaramide, melting between 168° and 175°. This body is insoluble in ether, slightly soluble in water and absolute alcohol, but dissolves easily in spirits of wine of 75 per cent. The aqueous solution is decomposed by heat.

The fumaric acid is probably formed by the action of water on monobromosuccinimide. This may show why no monobromosuccinimide could be obtained—

$$CHBr.CH_2(CO)_2NH + 2HOH = (CH.COOH)_2 + NH_4Br.$$

W. C. W.

On some New Carbamates. By DRECHSEL (*J. pr. Chem.* [2], xvi, 180—200).—1. *Ammonium Carbamate.*—By passing carbonic acid gas into milk of lime previously diluted with 3—4 times its volume of strong aqueous ammonia, a clear liquid is obtained, which is decomposed on heating, with separation of calcium carbonate, and by sodium carbonate with immediate precipitation of the same. Carbamic acid is thus formed by the union of carbonic anhydride and ammonia gases in presence of water. We have here proof that the affinity existing between these gases is greater than that between lime and carbonic anhydride, and strong grounds for regarding aqueous ammonia as simply a solution of the gas in water. Ammonium carbamate in solution is slowly converted into the carbonate. The conversion is, however, incomplete, and is much impeded by the presence of free ammonia. Even on long boiling of its solution, the carbamate is not completely decomposed, and in presence of ammonia it is comparatively stable. While this compound thus passes more or less readily into ammonium carbonate so inversely the latter salt in aqueous solution parts with the elements of water and is converted into the carbamate.

2. *Calcium Carbamate*, $2(NH_2.CO_2)_2Ca + H_2O$.—Interesting details of the preparation of this salt are given. It forms a fine powder, revealing under the microscope the presence of small flat prisms. From its saturated solution in warm aqueous ammonia, in which form it exhibits considerable stability, it crystallises, when cooled to 0°, in beautiful four-sided prisms. In aqueous solution this salt is extremely unstable. When newly prepared, it is entirely without smell; but an ammoniacal odour soon becomes perceptible, the salt entering into decomposition with its own water of crystallisation. Heated to 95—100° in an air-bath it is partially decomposed; after some time the weight becomes constant, the residue amounting to 76·56 per cent. of the weight of carbamate taken, and consisting of a mixture of calcium carbonate and carbamate. This result entirely conforms to the equation—

$$2\{NH_2.CO.O\}_2Ca + H_2O = NH_2.CO_2.NH_4 + \underbrace{\{NH_2.CO.O\}_2Ca + CaCO_3}.$$

The anhydrous salt exhibits decomposition on being heated to the softening point of ordinary glass. This occurs according to the equation $\{NH_2.CO.O\}_2Ca = CaCN_2 + 2H_2O + CO_2$, calcium cyanide being formed.

3. *Strontium Carbamate*, $\{NH_2.CO.O\}_2Sr$, occurs in the form of minute shining plates. The dry salt, being anhydrous, is much more stable than the calcium salt, which in other respects it entirely resembles.

4. *Barium Carbamate* was obtained only in the form of the double salt which it forms with barium chloride, viz., $\{NH_2.CO.O\}_2Ba.BaCl_2$.

5. *Lithium Carbamate*.—The author's attempts to prepare this compound were unsuccessful.

6. *Sodium Carbamate* crystallises with water in beautiful prisms which effloresce rapidly in the air, and quickly lose their water of crystallisation over sulphuric acid. In the anhydrous state they are permanent. The crystalline and anhydrous salts are decomposed on heating according to the following equations:—

1. Crystalline salt...... $2(NH_2.CO.ONa) + xH_2O = Na_2CO_3 + NH_2.CO.ONH_4 + (x - 1)\ H_2O.$
2. Anhydrous salt...... $NH_2.CO.ONa = NCO.Na + H_2O.$

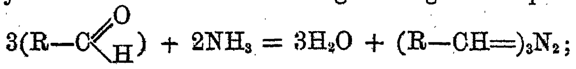
7. *Potassium Carbamate*, $NH_2.CO.OK$, has been prepared by the author according to several methods. It occurs in small needles and prisms, which are deliquescent. The decomposition of the anhydrous salt by heat is entirely analogous to that of the sodium salt. In neither case is the formation of cyanamide observed. That this should occur in the case of the carbamates of the alkaline earths, is explained by a secondary decomposition of the cyanates of the latter, which are first formed. Similarly ammonium carbamate yields urea as a product of its decomposition by heat, mediately through the cyanate. All the carbamates, therefore, hitherto investigated exhibit uniformly this decomposition into a cyanate and water. This dehydration is regarded by the author as identical in kind with that which determines the conversion of amides into nitrils, and the constitution of the resulting cyanates as therefore identical with that of cyanetholin, thus:—

$$CO\begin{cases} NH_2 \\ OR' \end{cases} = C\begin{cases} N''' \\ OR' \end{cases} + H_2O.$$

C. F. C.

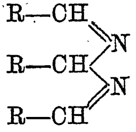
Furfuramide and Furfurine. By R. Schiff (*Deut. Chem. Ges. Ber.*, x, 1186—1193).—The ammonia derivatives of a certain class of aldehydes have long been known to be capable of being converted by heat or by boiling alkaline solutions into similarly constituted bodies, which, however, differ from them in stability and other properties. Similar reactions are seen in the conversion of hydrazobenzene into benzidine, and of methyl-aniline into toluidine. The relation of these reactions to the above-mentioned molecular changes must be gained from a study of the hydramides, and the bodies which are isomeric with them.

The hydramides are formed according to the general equation—



$$3(R—C\begin{matrix}\diagup O \\ \diagdown H\end{matrix}) + 2NH_3 = 3H_2O + (R—CH=)_3N_2;$$

and they have hitherto been represented by the constitutional formula—



Hydracetamide, which is formed in a similar manner, is also represented by a similar formula ($R = CH_3$).

But the aromatic hydramides (such as hydrobenzamide) and furfuramide, &c., are unstable in presence of acids, while hydracetamide yields two series of salts with strong mineral acids, so that the supposition of an analogous constitution between hydrobenzamide and hydracetamide may well be questioned.

The author has investigated furfuramide and furfurine with the view of throwing light on the constitution of the hydramides and their isomerides.

Preparation of Furfuramide.—The best method is that of Fownes, by acting on aqueous furfurol with ammonia. Furfurine is obtained by bringing pure dry furfuramide (m. p. 117°) into contact with boiling dilute caustic potash. Pure furfurine melts at 116°, instead of 100°, as stated by Fownes.

Action of Acetic Anhydride on Furfurine.—Monacetyl-furfurine, $C_{15}H_{11}(C_2H_3O)N_2O_3$, is produced in the form of small, white, flocculent crystals, insoluble in water, and moderately soluble in alcohol and ether.

Acetyl-furfurine is an exceedingly stable body. It is decomposed by fusion with caustic potash. Heated to 240° it becomes charred, and at 250° melts and decomposes. The basic properties of the furfurine are perfectly lost in this derivative; it is not altered by dilute acids, but is decomposed by concentrated nitric acid.

The acetyl group is undoubtedly united to the nitrogen-atom, but a second hydrogen-atom does not seem to be present in this position, since ethyl and methyl iodides have no further action on acetyl-furfurine. It is not altered by being brought in contact with sodium in boiling xylene, and nitrous acid has no effect upon it.

When furfurine is warmed with carbon bisulphide, and left in contact with it for a long time, it turns red, but suffers no further alteration. Chloroform and alcoholic solution of caustic potash yield no trace of a body resembling the carbylamines.

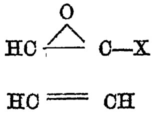
Furfurine and Nitrous Acid.—A yellowish crystalline body is formed, which is insoluble in water and ether, but easily soluble in alcohol. It melts at 94—95° to a red liquid, which consists of $C_{30}H_{27}N_5O_{15}$. This body, treated with hydrochloric acid and platinic chloride, yields a fine platinochloride, $(C_{30}H_{27}N_5O_{15}HCl)_2PtCl_4$. With ammoniacal solution of silver nitrate it forms a double salt which is not altered by light. When an absolute ethereal solution of furfurine is saturated with N_2O_3, in the absence of every trace of moisture, a small quantity of a very unstable body is obtained, which becomes dark-coloured at 82°, and slowly chars.

Furfuramide and Nitrous Acid.—Furfurol and ammonium salts are separated, but the reaction goes further. The ethereal solution of furfurol saturated with N_2O_3 deposits nothing on standing, but if the ether is allowed to evaporate spontaneously, a violent reaction begins when it has nearly disappeared. The red syrupy residue grows warm, streams of nitric oxide escape, and a red oil is left, which finally solidifies, yielding a body with strongly acid properties. This phenomenon occurs only when small quantities of furfurol (3 to 4 grams) are operated upon. If a larger quantity (*e.g.*, 10 grams) is used, as soon as the ether has evaporated, a flame is suddenly observed, about a metre in height, accompanied by steam or smoke, and a porous mass of carbon is left behind. Furfurine is not attacked by nascent hydrogen or by the thiocarbimides (mustard oils).

Action of Thiocarbimides on Furfuramide.—(1.) With allylic thiocarbimide. Fine silky-white needles are obtained, insoluble in water, but soluble in alcohol and partly so in ether. They melt at 118°, and are decomposed at 135°. The composition of these crystals is $C_{15}H_{12}N_2O_3.CSNC_3H_5$. (2.) With phenylic thiocarbimide a well crystallised snow-white compound is formed, consisting of $C_{15}H_{12}N_2O_3.CSNC_6H_5 + H_2O$. This body is insoluble in water. It may be heated to 100° without loss of weight.

Aldehydes do not seem to form any compounds with furfuramide and furfurine.

Action of Bromine on Acetyl-furfurine.—The product is hexbromacetyl-furfurine, a yellowish-white powder, which is dissolved by acetic acid, and reprecipitated of a lighter colour on addition of water. It dissolves in alcohol, but suffers decomposition, the alcohol taking up hydrobromic acid. The formula of this body is $C_{15}H_{11}N_2O_3 + C_2H_3O + CBr$. The formula assigned by the author to the "furfur" group is—



In pyrrol the carbon-atom connected with group X is replaced by >NH, the presence of which, and the absence of an NH_2 group, remain to be proved. Experiments on this point have been begun, and it has been found that aldehydes, thiocarbimides, and bisulphide of carbon do not act upon pyrrol. G. T. A.

Distillation of Benzene, Toluene, and Xylene by Steam. By A. NAUMANN (*Deut. Chem. Ges. Ber.*, x, 1421). When the above-mentioned hydrocarbons are distilled by means of steam, the proportion of water and hydrocarbon which pass over, and also the boiling point, remain constant so long as the mouth of the tube which conducts the steam into the boiling liquid remains wholly in the hydrocarbon. They are also independent of the rate of distillation, of the height of the liquid above the point at which the steam enters, and of the space above the liquid occupied by vapour; when, however, the level of the condensed water reaches the mouth of the tube, the temperature and proportion of the liquids in the distillate is no longer constant.

The results with regard to the boiling points are as follows:—

	Temperature at boiling point.				
	Of mixed liquid.	Of mixed vapours.	Diff.		B.P.
Benzene and water	= 68·5	69·1	·6	Benzene only	79·5
Toluene „ „	= 82.4	84·1	1·6	Toluene „	108·5
Xylene „ „	= 89·0	91·5	2·5	Xylene „	135·5

The boiling point is in all cases below that of the lower-boiling liquid, owing to the attraction of unlike molecules being less than those of like molecules, as is also shown by the fact that the liquids are not miscible. The difference between the temperatures of the liquid and of the vapour increases as the boiling point approaches that of water. Proportion of liquids in the distillate:—

	H_2O.	C_6H_6.	C_7H_8	C_8H_{10}.
Volume....	100	8·5	21·2	44
Molecules..	100	2·4	·79	56
	9·41	1	—	—
	1·24	—	1	—
	1·78	—	—	1

The relation 0·41 : 1·24 : 1·78 = 1 : 3 : 4, the author considers to be merely accidental. He hopes from these and further results to be able to draw conclusions as to the molecular constitution of the vapours.

T. C.

Reduction of the Aromatic Hydrocarbons. By BERTHELOT (*Compt. rend.*, lxxxv, 831—836).—The final product of the reduction of benzene by hydriodic acid is hexane, C_6H_{14}, boiling at 69°, whilst C_6H_8, C_6H_{10}, and C_6H_{12}, are formed as intermediate products.

To explain this, the author supposes benzene to consist of one molecule of acetylene saturated with two others. Thus, $C_2H_2(C_2H_2)(C_2H_2)$, these two latter molecules being capable in their turn of uniting separately into hydrogen, to form the above bodies. L. T. O'S.

Preparation of Pentabromotoluene. By M. GUSTAVSON (*Bull. Soc. Chim.* [2], xxviii, 347).—The author gives certain details of the preparation of pentabromotoluene by the action of bromine on toluene in presence of aluminium bromide. The proportion in which the reagents should be employed are expressed by the ratio $C_7H_8 : 5Br_2$, care being taken to have the bromine in slight excess. Results approaching the theoretical are obtained. The reaction may even be recommended for the preparation of gaseous hydrobromic acid; in this case benzene may, of course, be substituted for toluene. The pentabromide is easily soluble in benzene, from which it crystallises in long needles, melting at 282—283°. C. F. C.

Action of Bromine on Cymene. By M. GUSTAVSON (*Bull. Soc. Chim.* [2], xxvi, 346—7). By the action of excess of bromine, in presence of aluminium bromide, upon cymene (b. p. 174—175°) toluene pentabromide and isopropyl bromide are formed. The reaction, which takes place at 0°, is represented by the equation, $C_{10}H_{14} + 5Br_2 = 4HBr + C_3H_7Br + C_7H_3Br_5$, and is a striking instance of the decomposition, at a comparatively low temperature, of an aromatic hydrocarbon, with formation of a body belonging to the methyl series.

The products of the decomposition are obtained in quantities corresponding almost exactly with those required by the above equation. The toluene pentabromide obtained melts at 282—283°; the isopropyl bromide boils at 60—63°.

The formation of isopropyl bromide in this reaction may be explained on two hypotheses. *First*, that the cymene employed has the constitution of isopropyltoluene, and is resolved by the action of bromine into its constituent radicles. *Secondly*, that the bromide in question is formed by the addition of HBr to propylene, this body being produced according to the equation, $C_{10}H_{14} + 5Br_2 = C_7H_3Br_5 + 5HBr + C_3H_6$. The author inclines to the latter view. C. F. C.

Cymene-Derivatives. By E. v. GERICHTEN (*Deut. Chem. Ges. Ber.*, x, 1249—1252). Chlorine acts readily upon cymene (from camphor) in presence of iodine to form a nearly colourless *chlorocymene*, of sp. gr. 1·014 at 14°, boiling at 208—211°. This product yields, by oxidation with dilute nitric acid, a *chlorotoluic acid*, crystallising in large laminæ, m. p. 194—195°. The acid dissolves sparingly in hot water, easily in alcohol. Its *barium salt*, $[C_6H_3Cl(CH_3)COO]_2Ba + 3H_2O$, crystallises in fine needles.

The *calcium salt*, $[C_6H_3Cl(CH_3)COO]_2Ca + 3H_2O$, forms crystalline nodules. By fusion with potash the acid yields an *oxytoluic acid*, which gives an intense violet coloration with ferric chloride.

Cymene yields, by Fittica's process, a nitro-compound which crystallises in snow-white needles, melting at 124·5°. The nitro-compound dissolves rapidly in warm strong sulphuric acid, and on pouring the solution into cold water, there is deposited a large quantity of white flocks, consisting, not of cymenesulphonic acid, as might be expected, but of *p*-toluic acid, melting at 177—178°. The formation of this last substance is not due simply to oxidation of the propyl-radicle at the expense of the nitro-group, but to a much more complicated reaction, which is being further investigated.

A dichlorocymene, boiling at 240—244°, is also formed by the action of chlorine upon cymene. J. R.

On the Action of Sodium upon Halogen-substitution Products of Aniline. By R. ANSCHÜTZ and G. SCHULTZ (*Deut. Chem. Ges. Ber.*, x, 1802—1804). The authors find that by the action of sodium upon ortho- and meta-chloraniline, as they have previously found in the case of the para-compound, azobenzene is formed. They regard the reaction as occurring in three stages, expressed by the equations—

$$\begin{aligned}
&(1.)\ 2(C_6H_4Br.NH_2) + Na_2 &&= 2(C_6H_4.Br.NH.Na) + H_2\\
&(2.)\ C_6H_4.Br.NH.Na + H_2 &&= C_6H._5NHNa + HBr \text{ and}\\
&(3.)\ 2(C_6H_5.NH.Na) + O_2 &&= C_{12}H_{10}N_2 + 2NaOH.
\end{aligned}$$

The substitution by Na of the H of the NH_2 group of bromaniline is probably determined by the presence of the Br atom in the benzene molecule. The authors have independently corroborated equation (3) by an observation upon $C_6H_5.NHK$, which they have succeeded in converting into azobenzene, by subjecting it to the action of a stream of air in presence of ether.

The authors are engaged in extending this reaction to the production of azo-compounds generally. C. F. C.

Decomposition of Parabromaniline by Heat. By R. Fittig and E. Büchner (*Liebig's Annalen*, clxxxviii, 23—30). Pure parabromaniline melts at 63° to a colourless liquid, which when more strongly heated, suddenly assumes a deep purple colour; at 190° a colourless liquid begins to distil, the boiling point rising steadily to 270°, when a dark solid is left behind. The volatile product behaves on redistillation in a similar way, but the dark residue becomes less and less until at last only pure aniline distils. The residue consists of a small quantity of a colouring matter, dissolving in alcohol with a splendid blue colour, and a mixture of dibrom- and tribom-aniline, which were distilled off with steam, and separated by means of hydrochloric acid, in which the tribromo-compound is insoluble. The dibromaniline melts at 89—90°, and the tribromaniline at 119—120°.

When parabromaniline is heated for some hours with hydrochloric acid to 160°, it is also partly resolved into aniline, dibromaniline, and tribromaniline. This singular reaction is explained by the equations: $2C_6H_4BrNH_2 = C_6H_5NH_2 + C_6H_3Br_2NH_2$, and $C_6H_4BrNH_2 + C_6H_3Br_2NH_2 = C_6H_5NH_2 + C_6H_2Br_3NH_2$. It is quite analogous to the decomposition of certain metallic chlorides by heat as: $2MoCl_3 = MoCl_2 + MoCl_4$, and $3WCl_4 = WCl_2 + 2WCl_5$. C. S.

Chlorobromaniline. By R. Fittig and E. Büchner (*Liebig's Ann.*, clvxxviii, 14—23). When parabromonitrobenzene is reduced by tin and hydrochloric acid, a certain quantity of chlorobromaniline is always formed, which is most conveniently separated by crystallising the mixture of the free bases from alcohol. To the mother-liquor, which contains all the chlorobromaniline and some parabromaniline, hydrochloric acid and water are added. On distillation only the chlorinated base goes over as its hydrochloride is decomposed by water. The new base crystallises in colourless, glistening prisms, which are often an inch long; it is almost insoluble in cold water, sparingly soluble in boiling water, and freely in alcohol. It melts at 69—69·5°, and readily sublimes. This compound has previously been observed by Hübner and Alsberg, who believed it to be nitrobromaniline. Several chemists have already found that by the reduction of nitro-compounds with tin and hydrochloric acid chlorinated amido-compounds are formed. Beilstein and Kuhlberg think that this is due to the action of stannic chloride, while Jäger believes that a nitro-compound may be formed, which is then decomposed by hydrochloric acid, and Hübner regards the nitro-compounds as oxidising agents, which liberate chlorine from the hydrochloric acid.

In order to test these different views, the authors made a series of experiments, in which they found that the quantity of chlorobromaniline increases when the reaction goes on very violently, whereas when the nitrobromobenzene is gradually added to a boiling solution of stannous chloride and hydrochloric acid, only parabromaniline is produced. When bromonitrobenzene is heated with concentrated nitric acid to 100° for 16 hours, no reaction takes place, and bromaniline is also not changed under the same conditions; but at 160° it is partially converted into dibromaniline (*see* last abstract). Chlorobromaniline is, however, readily obtained by passing chlorine into a hot solution of parabromaniline in concentrated hydrochloric acid. At the same time a dichlorbromaniline is formed, which does not combine with hydrochloric acid, dissolves readily in alcohol, and separates from it in large, probably monoclinic crystals melting at 93·5° to a deep red liquid, which on solidifying again becomes colourless. From these results it appears that, during the reduction of the nitro-compound, some of the nascent oxygen liberates chlorine, which then exerts a substituting action. C. S.

Dichloracetanilide. By C. O. CECH (*Deut. Chem. Ges. Ber.*, x, 1265—1267).—In a former paper (*Deut. Chem. Ges. Ber.*, ix, 337; abstract, *Journ. Chem. Soc.*, 1876, i, 710) the author described a substance formed by the action of aniline on chloral cyanide-cyanate, which he then represented as an anilide of chloral, $COH—CCl_2.NHC_6H_5$. Pinner and Fuchs (*Deut. Chem. Ges. Ber.*, x, 1063; abstract, *Journ. Chem. Soc.*, 1877, ii, 584) afterwards obtained the same substance by the action of aniline acetate on chloral acetyl-cyanide, and came to the conclusion that it is the anilide of dichloracetic acid. The author has now succeeded in preparing dichloracetanilide directly by the action of phosphoric anhydride on aniline dichloracetate, and finds that it is identical with the body first obtained by him as above. He has, therefore, established the correctness of the conclusion arrived at by Pinner and Fuchs as to the constitution of the body.

Dichloracetanilide may also be obtained by the action of aniline on dichloracetamide. J. R.

Condensation-products of Tertiary Aromatic Bases. By OTTO FISCHER (*Deut. Chem. Ges. Ber.*, x, 1623—1626).—1. *Phthalein of Monobromodimethylaniline.* — Bromodimethylaniline heated with phthalic chloride, yields a base, the hydrochloride of which crystallises from alcohol in feathery steel-blue needles having the formula $C_{24}H_{22}Br_2N_2O_2.HCl$. This salt dissolves easily in alcohol, wood-spirit, chloroform, and glacial acetic acid, and sparingly in water. Strong acids dissolve it, with yellow coloration. The solution in strong hydrochloric acid deposits, on addition of water, a dirty green precipitate having the formula $C_{24}H_{22}N_2O_2Br_2.2HCl$. The base separated from the hydrochloride is of a bluish-violet colour, and easily soluble in alcohol and ether. Its ethereal solution gives with picric acid a green precipitate of *picrate*. The *platinum salt*, $2(C_{24}H_{22}N_2Br_2O_2.HCl).+PtCl_4$, is an indigo-blue crystalline powder.

2. *Benzaldehyde and Dimethylaniline.*—These substances act upon each other in presence of zinc chloride in the manner shown by the equation—

$$C_7H_6O + 2C_6H_5N(CH_3)_2 = C_{23}H_{26}N_2 + H_2O.$$

The base thus formed crystallises from alcohol in white needles melting at 92—93°, and dissolving easily in ether. It forms a *picrate*, $C_{23}H_{26}N_2.2C_6H_2(NO_2)_3OH$, which crystallises in yellow needles, and a *platinum salt*, $C_{23}H_{26}N_2.2HCl.PtCl_4$, which is white at first but turns green in the air. The other salts, especially when dissolved in alcohol, speedily undergo oxidation to bluish-green colouring matters of complex constitution.

3. *Furfurol and Dimethylaniline* react similarly, under the influence of zinc chloride, to form a white, crystalline, basic substance, which melts at about 70°. The composition of this body has not yet been determined with certainty. Its salts have the tendency to become oxidised to red colouring matters. J. R.

Derivatives of Diphenylamine. By R. GNEHM and G. WYSS (*Deut. Chem. Ges. Ber.*, x, 1318—1324).—*Tetranitrodiphenylamine.*—1 part of diphenylamine dissolved in 40 parts of glacial acetic acid is heated in a capacious flask with 3 to 5 times its weight of nitric acid. Red fumes are evolved, and the solution turns green. When the reaction is complete, excess of water is added, when a yellowish flocculent precipitate separates. On drying it forms a dirty greenish-yellow powder, forming a sticky mass when heated, and on cooling solidifies to a brown resinous body. It is purified by boiling with dilute sodium carbonate solution, from which it separates on cooling in brownish-yellow flocculent masses which melt at 150—170°. Methyldiphenylamine yields the same body when thus treated, and not a methylnitrodiphenylamine. The largest and purest yield is obtained by acting with 3 to 5 parts of nitric acid on 1 part of diphenylnitrosamine dissolved in 10 parts of hot glacial acetic acid.

When pure the new body crystallises from glacial acetic acid in fine yellow needles or prisms which melt at 192°, and on being more strongly heated in the air burns with ease, but does not explode. On analysis it was found to have the composition $NC_{12}H_7(NO_2)_4$. It is, therefore, tetranitrodiphenylamine, $NH.\{C_6H_3(NO_2)_2\}_2$, and consequently is isomeric with Austen's parapicrylmetanitraniline melting at 205° (*Chem. Soc. J.*, 1875, 165) and parapicrylparanitraniline melting at 216°.

Tetranitrodiphenylamine is soluble in alcohol, ether, and benzene, and crystallises from its solution in fine yellow needles or prisms. Like its isomerides it is easily dissolved by a hot solution of sodium or potassium hydrate, forming a magnificent scarlet solution, which on cooling deposits the body unaltered in red-brown minute needles. The authors were unable to obtain an acetyl-derivative, even by the action of hot acetyl chloride in pressure tubes.

Tetramidodiphenylamine.—When tetranitrodiphenylamine is reduced by means of zinc and dilute hydrochloric acid, it forms an easily soluble colourless salt, from whose aqueous solution sodium hydrate precipitates a colourless, flocculent, basic body. This the authors consider to be tetramidodiphenylamine, $NH.\{C_6H_3(NH_2)_2\}_2$, but they were unable to obtain it in a state fit for analysis. The solution in hydrochloric acid of the new base turns red-violet in the air; gives a violet colour with platinum chloride, gradually resolving into a dark precipitate; a dark violet with ferric chloride; a dark brown-red with zinc chloride, and with sodium nitrite a blue colour quickly turning red, and then resolving itself into a brown precipitate. By the addition of ammonia a colourless precipitate is formed, but on exposure to air the precipitate redissolves, and a splendid deep blue solution is formed, of very unstable character.

By the action of air the new base is readily oxidised, with probable formation of tetrimidodiphenylamine, the reaction being similar to the formation of diimidonaphthol from diamidonaphthol (*Ann. Chem. Pharm.*, cliv, 303).

Dinitrotribromodiphenylamine.—When a solution of 1 part of tetrabromodiphenylamine in 1 to 2 parts of nitric acid is heated, much nitrogen tetroxide and bromine is evolved, and on cooling a brown crystalline mass separates. By treatment with alcohol, glacial acetic acid, and sodium hydrate solution, different bodies are separated. The portion soluble in alcohol yields after repeated recrystallisations a new body which melts at 209—210°, and gives on analysis numbers agreeing with the formula $C_{12}H_6H_3Br_3O_4$. It is dinitrotribromodiphenylamine, $N.C_{12}H_6(NO_2)_2Br_3$. When pure it forms thin, glittering, yellow plates, soluble in ether to a reddish-yellow solution, and in benzene and chloroform with a yellow colour. It melts to a yellow liquid, and burns easily when strongly heated in the air. E. N.

Action of Primary Amines on Diphenylnitrosamine. By OTTO N. WITT (*Deut. Chem. Ges. Ber.*, x, 1309).—Diphenylnitrosamine and aniline react vigorously on one another at 70°, the temperature rising to upwards of 100°. Hydrogen is evolved, of very evil odour, a dark tarry mass being formed. If excess of aniline is employed, it is possible to isolate amidazobenzene, diphenylamine, and diazoamidobenzene from the products, but only with difficulty, on account of the tarry bye-products. If, however, paratoluidine be employed (4 parts to 1 of nitrosamine) *paradiazoamidotoluene*, melting at 115·5° to 116° is readily obtainable from the product by washing with dilute acetic acid and crystallisation from ligroïn. The body corresponded in all respects with pure paradiazoamidotoluene; it formed an amido-azoderivative on heating with hydrochloride of aniline, and when it was heated with alcoholic phenylenediamine, no coloration was developed (difference from diazo-bodies). On further adding acetic acid, an orange-red chrysoïdin was produced. From the mother-liquors diphenylamine, melting at 55°, was obtained. The reaction of the paratoluidine hence appears to be—

$$N(C_6H_5)_2NO + NH_2.C_7H_7 = H_2O + N(C_6H_5)_2N{=}N.C_7H_7$$

$$N(C_6H_5)_2N = N.C_7H_7 + NH_2.C_7H_7 = N(C_6H_5)_2H + C_7H_7.N{=}N.NH.C_7H_7.$$

When a mixture of diphenylnitrosamine and aniline hydrochloride in equal numbers of molecules with double the weight of aniline, is left to itself for some hours and then gently heated, an almost quantitative yield of amidoazobenzene is obtained by a parallel reaction, the diazoamidobenzene first formed being further acted upon by the aniline hydrochloride. At a higher temperature and with a larger excess of aniline, a different body is produced, crystallising in lustrous ruby needles, soluble in concentrated sulphuric acid, with an intense characteristic violet tint. The formation of this body was traced to the reaction of the diphenylamine set free in the earlier stage on the amidoazobenzene, the equation being—

$$2NH(C_6H_5)_2 + 2C_6H_4(NH_2).N_2.C_5H_5 = N\{N(C_6H_5)_2\}_2.C_6H_4.N_2.(C_6H_5) + NH_2.C_6H_5 + C_6H_4(NH_2)_2.$$

so that the new product is the saffranin of the series. The author regards it as the type of a new class of compounds containing 3 N-atoms linked together, to which he proposes to apply the term *triazo-derivatives.*

C. R. A. W.

Derivatives of Orthotoluidine. By A. LADENBURG (*Deut. Chem. Ges. Ber.*, x, 1260—1262).—In a former paper the author stated that he had obtained, by heating formotoluide, a substance agreeing in composition with the formula C_8H_9N. Further examination has shown that the substance is identical with *methenyldiorthotolyldiamine*, $C_{16}H_{16}N_2$, obtained by the action of phosphorus trichloride on formotoluide containing toluidine. The identity of the two products is shown by their crystallising in prisms which melt at the same temperature (150°); by their dissolving in dilute hydrochloric acid only on heating; by their platinum double salts having the same crystalline form; and by their behaving in the same manner with bromine, with which they combine to form a substance crystallising in yellow prisms, and having the formula $C_{15}H_{16}N_2Br_2$.

The author has also obtained *ethenyldiorthotolyldiamine*, $C_{16}H_{18}N_2$, by the action of phosphorus trichloride on orthotoluidine and glacial acetic acid. This substance crystallises in colourless needles, which dissolve easily in dilute hydrochloric acid and melt at 140·5°.

J. R.

A New Xylidine. By E. WROBLEVSKY (*Deut. Chem. Ges. Ber.*, x, 1248).—This substance was obtained by the following steps:—Purified isoxylene was converted first into nitro-compound, and then, by reduction, into xylidine. The xylidine was converted, by heating with acetic acid, into acetoxylidine (melting point 127°), and this product was heated with nitric and sulphuric acids, to form acetonitroxylidine, which crystallised from alcohol in colourless needles melting at 180°. The acetonitroxylidine, when heated with sulphuric acid, yielded solid nitroxylidine, which crystallised in red needles melting at 76°. This nitroxylidine gave by Griess's reaction a solid nitroxylene, which crystallised from alcohol in large flat needles (melting point 255°), and yielded by reduction a liquid xylidine of sp. gr. 0·9935 at 0°, boiling at 220—221°.

The following salts have been prepared:—

$C_8H_9NH_2.HCl$. Long colourless brilliant needles.

$C_8H_9NH_2.HNO_3$. Long white nacreous needles, soluble in 21 parts of water at 13°.

$(C_8H_9NH_2)_2H_2SO_4 + H_2O$. Long white needles.

The acetyl-compound, $C_8H_9NH(C_2H_3O)$, crystallises from alcohol in large flat needles, which melt at 144·5°. The constitution of this xylidine is not yet made out. J. R.

On the Bases $C_nH_{2n-3}ClN_2$. By O. WALLACH and F. OPPENHEIM (*Deut. Chem. Ges. Ber.*, x, 1193—1199).—The authors obtained from diethyloxamide a basic body of the composition $C_6H_9ClN_2$, to which the name of *chloroxalethyline* was given (this *Journal*, 1877, ii, 184). In order to determine whether it is possible to remove the chlorine from this body by simple reactions, it was dissolved in petroleum-naphtha, and finely divided sodium was added to the solution. The following equation represents the results of the reaction:—

$$2C_6H_9ClN_2 + Na_2 = C_{12}H_{18}N_4 + 2NaCl.$$

The base $C_{12}H_{18}N_4$ may be called *dioxalethyline*. When bromine is added to a solution of chloroxalethyline in carbon disulphide or chloroform, it is eagerly absorbed, and a reddish crystalline mass is formed, which can be separated into two parts by crystallisation. The larger of these consists of red needles, melting at 112·5—113·5°: the other part forms fine red crystals, melting at 132—133°, the crystallographic measurements of which are given in the paper. Both these bodies are soluble in chloroform, carbon disulphide, and alcohol, but not in cold water. Hot water dissolves them, with decomposition. The following formulæ show their composition:—

Tetrabromide ...... $C_6H_9ClN_2Br_4 = C_6H_8ClBrN_2.Br_2.BrH$
Tribromide .... $C_6H_9ClN_2Br_3 = C_6H_8ClBrN_2.Br_2$

Both compounds yield the same base when boiled with water. This base, $C_6H_8ClBrN_2$, may be called *bromochloroxalethyline*. It is sparingly soluble in water, but dissolves in alcohol, and possesses a peculiar aromatic odour. It forms fine crystalline salts. In addition to the hydrobromic acid salt (which is very hygroscopic) the following salts were obtained: the hydrochloric acid salt in hydrated prisms, the nitric acid salt in small curved needles, the platinum salt, $(C_6H_8ClBrN_2.HCl)_2PtCl_4$, in fine plates. The silver salt—

$$(C_6H_8ClBrN_2)_2NO_3Ag,$$

is very characteristic. It may be obtained by mixing an aqueous solution of the base with silver nitrate. It crystallises from dilute alcohol in remarkably well formed, transparent, glassy prisms. Salts of the base may also be formed from other metallic salts.

The bromine of the free base seems to be as intimately united as the chlorine. It is scarcely acted on by aqueous and alcoholic solutions of potash, but is perfectly decomposed by distillation. There is a striking analogy between the halogen-derivatives of chloroxalethyline and of nicotine, as the following table shows:—

Derivatives of oxalethyline.	Derivatives of nicotine.
$C_6H_{10}N_2$	$C_{10}H_{14}N_2$
$C_6H_8Br_2N_2.Br.HBr$	$C_{10}H_{12}BrN_2.Br_2.HBr$
$C_6H_8Br_2N_2.Br_2$	$C_{10}H_{12}Br_2N_2.Br_2$
$C_6H_8Br_2N_2.HBr$	$C_{10}H_{12}Br_2N_2.HBr$.

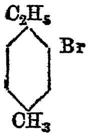
Iodine unites with chloroxalethyline in the same way as bromine does. G. T. A.

Xylene Sulphamides. By IRA REMSEN (*Deut. Chem. Ges. Ber.*, x, 1199—1200).—The author has described the preparation of the sulphoxylenes in a previous paper. It has since been found that the perfect separation of the xylenesulphamides is not so easy as at first appeared to be the case. Three bodies have been isolated from the crude product. The first of these melts at 132°; the second at 110°. These two are both derived from isoxylene. The third body has not been obtained in a state of purity, and it is not known whether it is a derivative of para- or of isoxylene. The *amide*, which melts at 132°, yields, when distilled alone or with lime, a body which is insoluble in water, but crystallises from alcohol. It has not yet been examined.

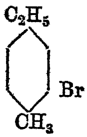
Oxidation of a mixture of the amide melting at 110° with the third amide yielded parasulphaminetoluic acid, together with a second acid with similar properties.

Most of the tri-derivatives of benzene are found to split up on oxidation into the simplest products.

Bromoparaxylene yields on oxidation a monobasic acid, bromoparatoluic acid, which shows that the bromine-atom prevents the oxidation of one of the methyl groups. The bromine protects the group to which it holds the ortho position. Bromethyltoluene may be either—



or



From the first formula oxidation should produce an acid—

$$C_6H_3.C_2H_5.Br.COOH:$$

from the second, $C_6H_3.CH_3.Br.COOH$. G. T. A.

Compounds of Elements of the Nitrogen Series with Aromatic Organic Radicles. By A. MICHAELIS and E. BENZINGER (*Liebig's Annalen*, clxxxviii, 275—292).—This section of the author's researches treats of the derivatives of benzenephosphonic acid, which bears to phosphoric acid the same relationship that benzenesulphonic acid does to sulphuric acid:

$$PO(OH)_3 \qquad\qquad SO_2(OH)_2$$

$$PO\left\{\begin{matrix}C_6H_5\\(OH)_2\end{matrix}\right. = C_6H_5.PO_3H \qquad SO_2\left\{\begin{matrix}C_6H_5\\OH\end{matrix}\right. = C_6H_5.SO_3H.$$

The authors apply to it the term *phosphenylic acid.*

Benzenephosphonic acid dissolves in nitric acid without alteration even when heated; but on heating it with 7 parts of fuming acid in sealed tubes to 100—110° for 5 or 6 hours, nitration takes place, little but *nitrobenzenephosphonic acid* (nitrophosphenylic acid) being formed, $C_6H_4(NO_2).PO_3H_2$. A white solid mass is left when the contents of the tubes are evaporated to dryness; this is best purified by converting it into barium salt by means of barium carbonate, and treating the product with cold water till nothing more is dissolved; benzenephosphonate of barium is then left undissolved. On concentrating the filtrate on the water-bath, brilliant yellow plates of *nitrobenzenephosphonate of barium* separate, containing $C_6H_4(NO_2).PO_3Ba,2H_2O$, three-fourths of the water of crystallisation being lost at 180°, while the remainder is expelled only at a higher temperature at which decomposition commences. From this salt the free acid is obtained by decomposition with sulphuric acid and treatment of the product with ether; it crystallises from water in cauliflower-like masses, from ether in white symmetrically arranged needles, very soluble in water, and highly deliquescent. When dry it is quite white, but the aqueous solution is strongly coloured yellow, leaving a white residue on evaporation to dryness; 100 parts of water at 22° dissolve 98 of acid; at 98°, only 92 parts are taken up: the barium salt also is more soluble in cold than in hot water. Alcohol and ether readily dissolve nitrobenzenephosphonic acid, but it is insoluble in benzene; it melts at 132°, the fused mass solidifying at 105°; at upwards of 200° it explodes, the odour of nitrobenzene being evolved and much carbon being left; hence in making a combustion of it, it is necessary to mix it thoroughly with finely divided copper oxide. When it is fused with soda-lime, aniline is evolved, the acid first splitting up into nitrobenzene and phosphoric acid (just as benzenephosphonic acid forms benzene and phosphoric acid), and the nitrobenzene being subsequently altered by the soda-lime; fusion with caustic potash forms a dark-red product soluble in water with the same colour; the colouring material is not taken up by ether or by alcohol after passing in carbon dioxide and evaporation to dryness.

The alkali-salts of nitrobenzenephosphonic acid are readily obtained by neutralising the acid with the appropriate alkali; they are readily soluble and do not crystallise; those of the alkaline earths are difficultly soluble and are crystallisable. Besides the neutral salt, an acid *barium* salt exists $\{C_6H_4(NO_2).PO_3H\}_2Ba,2H_2O$; this is obtainable from the neutral salt by treatment with enough sulphuric acid to withdraw half the barium present; it is more soluble in water and less readily crystallisable than the neutral salt; alcohol takes up traces of it. The *calcium salt*, $C_6H_4(NO_2).PO_3Ca.\frac{1}{2}H_2O$, when dried over sulphuric acid, may be obtained as an amorphous powder by neutralising the free acid with marble-powder, collecting the insoluble mass, dissolving it in water, evaporating the filtered liquid to a small bulk on the water-bath, and finally leaving it over sulphuric acid in a vacuum. The *silver salt*, $C_6H_4(NO_2).PO_3Ag_2$, is amorphous, as is also the *lead salt*, $C_6H_4(NO_2).PO_3Pb$; these are obtainable from the neutral alkaline salts by double decomposition as precipitates; from a neutral solution of sodium nitrobenzenephosphonate, barium chloride throws down a white crystalline precipitate on boiling; lead acetate, a white precipitate soluble in nitric or hot acetic acid; ferric chloride, a red precipitate, soluble in hydrochloric acid; copper sulphate, a slight precipitate in the cold, becoming much more copious on boiling, and soluble in much acetic acid. Cobalt nitrate on slightly warming gives a violet precipitate soluble in hydrochloric acid; bismuth nitrate, a white flocculent precipitate soluble in hydrochloric acid, insoluble in acetic acid; mercuric chloride, a white flocculent precipitate; and zinc chloride, a white precipitate, soluble in hydrochloric acid on warming, and re-precipitated by addition of ammonia.

By the action of nascent hydrogen (tin and hydrochloric acid) nitrobenzenephosphonic acid is readily converted into *amidobenzenephosphonic acid* (amidophosphenylic acid), $C_6H_4(NH_2).PO_3H_2$, crystallisable in white shining needles, soluble in hydrochloric acid, sparingly soluble in water (0·43 part in 100 at 20°, 0·52 at 100°), and insoluble in alcohol and ether. When heated it does not fuse, but turns bluish-green at 280° with decomposition; heating with soda-lime splits it up into phosphoric acid and aniline, thus :—

$$C_6H_4(NH_2).PO(OH)_2 + H_2O = C_6H_5.NH_2 + PO(OH)_3.$$

With hydrochloric acid it does not form any stable isolable compound; although it readily dissolves in that acid, the solution furnishes nothing but unaltered amidobenzenephosphonic acid on spontaneous evaporation over lime. Amidobenzenephosphonates of the alkaline earths and alkalis are readily soluble in water; the lead, silver, and copper salts, respectively, $C_6H_4(NH_2).PO_3Pb$, $C_6H_4(NH_2).PO_3Ag_2$, and $C_6H_4(NH_2).PO_3Cu$, are obtained as precipitates by double decomposition.

Sodium amalgam and nitrobenzenephosphonic acid do not form azo- or hydrazo-benzenephosphonic acid, the main product being the sodium salt of amidobenzenephosphonic acid, $C_6H_4(NH_2).PO_3Na_2 3H_2O$. From this the acid is obtained by addition of lead acetate, and decomposition of the precipitated lead-salt by sulphuretted hydrogen.

Diazobenzenephosphonic nitrate or *Diazophosphenylic nitrate*, $C_6H_4N_3O_3.PO_3H_2 = C_6H_4<\begin{matrix}N{=}NO_3\\PO_3H_2\end{matrix}$ or $C_6H_3(NO_2)<\begin{matrix}N{=}NO.H\\PO_3H_2\end{matrix}$. This is an acid compound produced by the action of nitrous acid on a solution of amidobenzenephosphonic acid in nitric acid. It forms well-defined prisms containing $3H_2O$, melting at 188°, and exploding at slightly higher temperatures; 100 parts of water dissolve 57·82 parts at 18°, 59·03 at 80°, the solutions being yellow; in alcohol it is readily, in ether sparingly, soluble. On boiling it with water alone, no formation of nitric acid is noticeable, nor is any produced by the further addition of sulphuric acid; but on boiling with caustic soda, a dark-red colour is developed which almost disappears on addition of sulphuric acid; nitric acid can then be readily distinguished in the liquid. The salts which it forms with the alkalis and alkaline earths are soluble and crystallisable; those of the heavy metals for the most part insoluble and red or yellow; they are all explosive. The *sodium salt*, $C_6H_4N_3O_3.PO_3Na_2 + 2H_2O$, is precipitated as a yellow crystalline substance on adding alcoholic caustic soda to a concentrated solution of the acid in absolute alcohol; it is almost insoluble in alcohol, but readily soluble in water, and crystallisable therefrom. The *potassium salt*, $C_6H_4N_3O_3.PO_3K_2 + 2H_2O$, is similarly obtained, and possesses the same properties. The *barium salt*, $C_6H_4N_3O_3.PO_3Ba + 3H_2O$, is obtained by neutralising the acid with barium carbonate, dissolving the sparingly soluble salt in water, and concentrating first over the water-bath, then in a vacuum over sulphuric acid; it forms reddish-yellow shining needles. The *silver* and *lead salts*, $C_1H_4N_3O_3.PO_3Ag_2$ and $C_6H_4N_3O_3.PO_3Pb$, may be obtained as amorphous precipitates by adding the corresponding metallic salts to an alkaline salt of the acid.

It is noticeable that of the 3 mols. of water of crystallisation in the free acid, only 2 are lost at 130°, the third not being expelled until a temperature is reached at which the acid begins to decompose: hence the monohydrated acid may be regarded as $C_6H_4(NO_2)\begin{cases} N{=}NH(OH)_2 \\ PO_3H_2 \end{cases}$ if the acid be viewed as containing the nitro-phenyl group $C_6H_4(NO_2)$. In general properties this diazo-derivative is different from most members of the diazo-group hitherto described, especially in not evolving hydrogen and forming an oxy-acid on boiling with water or alkalis. Experiments on the action of reducing agents are contemplated with a view to determine which of the above two formulæ correctly represents the substance. C. R. A. W.

Azophenetol. By E. HEPP (*Deut. Chem. Ges. Ber.*, x, 1652).— This substance is produced by the action of reducing agents on nitrophenetol. It is best obtained by heating an alcoholic solution of nitrophenetol (1 : 4) with potash and zinc-dust, and filtering the liquid while hot. The azophenetol (1 : 4) is deposited, as the solution cools, in small orange-yellow laminæ, which melt at 175° and afterwards distil without decomposition. It is insoluble in water, but dissolves easily in ether, benzene, and hot alcohol. The numbers obtained by analysis agree with the formula—

$$C_2H_5O.C_6H_4.N{=}N.C_6H_4.OC_2H_5.$$

Similarly, nitrophenetol (1 : 2) yields azophenetol (1 : 2).

Azophenetol is also formed on treating the silver salt of azophenol with ethyl iodide. Conversely, azophenetol, when heated to 180° with hydrochloric acid in sealed tubes, yields azophenol, together with ethyl chloride. J. R.

Derivatives of Thymol. By A. Ladenburg and Th. Engelbrecht (*Deut. Chem. Ges. Ber.*, x, 1218—1225).—The *ethyl-ether of dinitrothymol* is obtained by heating the sodium salt to 140—150° in sealed tubes with ethyl iodide and alcohol. It crystallises in colourless tables, which melt at 52—53°, dissolve easily in alcohol and ether, and decompose when distilled.

The ether yields, by reduction with tin and hydrochloric acid, a body which is converted by distillation with dilute aqueous ferric chloride into oxythymoquinone and *dioxythymoquinone.*

Dinitrothymol reacts with phosphorus pentachloride, when heated therewith, to form *chlorodinitrocymene*, $C_{10}H_{11}Cl(NO_2)_2$. This substance melts at 100—101°, and is moderately soluble in alcohol and ether, less freely in carbon bisulphide and chloroform.

Chlorodinitrocymene is converted by reduction with tin and hydrochloric acid into an amido-compound, which, by oxidation with potassium bichromate and sulphuric acid, yields oxythymoquinone and *chloroxythymoquinone*, $C_6CH_3C_3H_7O_2OH$. The latter substance crystallises in lemon-yellow prisms, which melt at 122°, sublime very readily, and dissolve easily in alcohol and toluene. It dissolves in solution of potassium hydrate or carbonate, with fine violet colour, and is precipitated unaltered by hydrochloric acid. But on boiling the alkaline solution it is converted into *dioxythymoquinone* or *thymozarin.*

Dioxythymoquinone, $C_{10}H_{12}O_4$, crystallises from hot alcohol in prisms of a beautiful red colour, which melt at 220° and sublime without decomposition. It is only sparingly soluble in alcohol and water, but dissolves easily in ammonia and potash with violet colour. The same product had been previously obtained by the authors by boiling a concentrated solution of oxythymoquinone in potash.

According to Ladenburg, the foregoing facts afford a new and, he thinks, incontestable proof of his proposition, that benzene contains two pairs of symmetrically-combined hydrogen-atoms.

If the formula of thymol be written thus:

$$\begin{array}{ccccccc} & a. & b. & c. & d. & e. & f. \\ C_6 & CH_3 & C_3H_7 & OH & H & H & H \end{array}$$

that of chlorodinitroxycymene must be—

$$\begin{array}{ccccccc} & a. & b. & c. & d. & e. & f. \\ C_6 & CH_3 & C_3H_7 & Cl & NO_2 & NO_2 & H \end{array}$$

In whatever way the oxidation of the corresponding amido-compound is effected, the chlorine in the resulting chloroxythymoquinone will undoubtedly occupy the position *c;* consequently the dioxythymoquinone obtained from the last-named body will have the group (OH) in the same position, and its formula must be one of the three following:—

	a.	b.	c.	d.	e.	f.
C_6	CH_3	C_3H_7	OH	O	O	OH
C_6	CH_3	C_3H_7	OH	O	OH	O
C_6	CH_3	C_3H_7	OH	OH	O	O

On the other hand, since dioxythymoquinone may also be obtained from thymoquinone, by previous conversion into oxythymoquinone, and since thymoquinone from thymol must have one of its oxygen-atoms in the position *c*, it follows that dioxythymoquinone thus prepared must have one of the three following formulæ:—

	a.	b.	c.	d.	e.	f.
C_6	CH_3	C_3H_7	O	O	OH	OH
C_6	CH_3	C_3H_7	O	OH	O	OH
C_6	CH_3	C_3H_7	O	OH	OH	O

Now, in whatever way these six formulæ may be arranged, they lead direct to the above proposition, or (what the author, in his *Theorie der aromatischen Verbindungen,* has shown to be the same thing) to the necessary condition, that two of the hydrogen-atoms in benzene are symmetrical in regard to the other four. J. R.

Diatomic Phenol of Xylene. By CH. GUNDELACH (*Bull. Soc. Chim.* [2], xxviii, 342—346).—The author prepares the potassium salt of isochloroxylenesulphonic acid, $C_8H_8Cl.SO_3K + H_2O$, which he decomposes by fusion with potash; he thus obtains a body crystallising in small prisms, and exhibiting reactions similar to those of beta-orcin. This circumstance, together with the analogous formation of the latter compound from chloro-sulphocresylic acid, are regarded by the author as warranting the formula $C_8H_8(OH)_2$. C. F. C.

Action of Hydrochloric Acid upon Resorcin. By L. BARTH and H. WEIDEL (*Deut. Chem. Ges. Ber.*, x, 1464—1472).—By heating resorcin (20 grams) with fuming hydrochloric acid (25 c.c.) for some hours in sealed tubes to 180°, a resinous mass is obtained which exhibits a green metallic lustre in reflected light. From this the authors have isolated two bodies, A and B, its chief constituents:

(A.) A bright brownish-red amorphous powder, insoluble in water and in ether; slightly soluble in cold alcohol, easily soluble in hot alcohol and in glacial acetic acid. It is further dissolved by concentrated sulphuric acid, and is precipitated from this solution unchanged on dilution. Aqueous alkalis also dissolve it, forming a deep red solution, which exhibits a beautiful green fluorescence. The authors assign to this body the formula $C_{12}H_{10}O_3$.

By heating it with acetyl chloride to 100° in sealed tubes, a diacetyl substitution-product, $C_{12}H_8(C_2H_3O)_2O_3$, is obtained as a dark-brown powder. By fusion with potassium hydrate it is converted into resorcin. By heating it, according to the usual method, with zinc-dust, a distillate is obtained in small quantity, in which traces of benzene and diphenyl may be detected.

As the simplest representation of the reaction by which this dichroic resinous body is formed, the authors suggest the equation $2C_6H_6O_2 = H_2O + C_{12}H_{10}O_3$, and infer the following constitutional formula $(C_6H_4)_2O(OH)_2$. Deducing from this an obvious analogy to fluoresceïn, they have prepared a tetrabrominated derivative by the action of bromine upon the cold solution of the original substance in glacial acetic acid—in anticipation of its possessing colouring properties similar to those of Baeyer's eosin—which is essentially a brominated anhydride of resorcin. The compound was found, in effect, to possess tinctorial properties, but the colours communicated by it to fabrics were a brownish- and greyish-red, and decidedly lacked purity. Hence they conclude that while fluorescence is characteristic of bodies formed upon the type of anhydride, beauty and purity of colour follow only from the introduction of the phthalic acid residue.

(B.) A bright red amorphous powder, easily soluble in ether, alcohol, and glacial acetic acid, and to a certain extent in both cold and hot water. The aqueous alkalis dissolve this body to a brownish-yellow solution, which exhibits a blue fluorescence. Its empirical constitution is represented by the formula $C_{24}H_{18}O_5$. By heating it with acetyl chloride to 100° in sealed tubes, the diacetyl-product, $C_{24}H_{16}(C_2H_3O)_2O_5$, is obtained as a brown powder. By fusion with potassium hydrate, resorcin is regenerated. By the action of bromine upon the cold solution of this body in glacial acetic acid, a hex-substitution compound, $C_{24}H_{12}Br_6O_5$, is formed.

The authors express the reaction by which this second constituent of the original resin is formed, by the equation $4C_6H_6O_2 = 3H_2O + C_{24}H_{18}O_5$, from which, in conjunction with the above reactions, they infer the constitutional formula $(C_6H_4)_4.O_3.(OH)_2$.

Both ethers are vigorously acted upon by nitric acid; amorphous products are obtained as precipitates on the addition of water. After long boiling with nitric acid, until water no longer occasioned a precipitate, a crystalline powder was deposited on evaporation, which, after purification, was identified as isophthalic acid.

In conclusion, the authors recommend the original reaction with hydrochloric acid as an exceedingly delicate test for the presence of resorcin. This reaction is unaffected by the presence of pyrocatechin, and of the impurities which often accompany resorcin. C. F. C.

A New Mode of Formation of Hydroquinone. By E. HEPP (*Deut. Chem. Ges. Ber.*, x, 1654).—On adding hydroxylamine hydrochloride to a dilute aqueous solution of nitrosophenol in soda-ley, and gently warming the liquid, nitrogen is evolved and hydroquinone produced. The first product of the reaction is diazophenol, which breaks up into hydroquinone and nitrogen thus:—

$$C_6H_4(OH)NO + NH_2.OH = C_6H_4(OH)N{=}N.OH + H_2O;$$
$$C_6H_4(OH)N{=}N.OH = C_6H_4(OH)_2 + N_2.$$

J. R.

Actions of Amines upon Chlorinated Quinones. By G. NEUHÖFFER and G. SCHULTZ (*Deut. Chem. Ges. Ber.*, x, 1792—1793).—The objects of this investigation are to ascertain (1) in what respects the action of amines upon the quinones differs from their action upon ketones; and (2), whether this action is confined to monamines, or is common to the diamines, imides, and amides. From the solution of these questions the authors hope to be able to draw conclusions respecting the constitution of the quinonamines.

By the action of trichloroquinone upon aniline, the authors have obtained a compound crystallising in shining plates having a metallic lustre. The composition of this body is expressed by the formula $C_{18}H_{13}N_2ClO_2$. It appears, therefore, to be dianilidomonochloroquinone.
C. F. C.

Formula of Quinhydrone. By C. LIEBERMANN (*Deut. Chem. Ges. Ber.*, x, 1614—1618).—The formula, $C_{12}H_{10}O_4$, assigned to this substance by Wöhler and Laurent, was altered by Wichelhaus, in accordance with the results of his investigations, to $C_{18}H_{14}O_6$. Now, since quinhydrone is produced directly by mixing aqueous solutions of quinone and hydroquinone, and is the only product of the reaction, the first of these formulæ represents it as a compound of 1 mol. of quinone with 1 mol. of hydroquinone ($C_6H_4O_2 + C_6H_6O_2$), whilst the second represents it as a compound of 2 mols. of quinone with 1 mol. of hydroquinone ($2C_6H_4O_2 + C_6H_6O_2$).

In order to determine which of these is the true formula, the author mixed together aqueous solutions of quinone and hydroquinone, and weighed the quinhydrone precipitated. He thus found that (1) when the two substances were mixed in equivalent proportions, the amount of quinhydrone thrown down was somewhat less than that required by the formula, $C_{12}H_{10}O_4$ (owing to its being soluble to a slight extent in water), but greater than that required by the formula, $C_{18}H_{14}O_6$; (2) when the substances were mixed in the proportion of 2 mols. of quinone to 1 mol. of hydroquinone, the quantity of quinhydrone thrown down was less than corresponded with either formula.

Moreover, on testing the filtrate from the quinhydrone, he found that, in the first case, neither quinone nor hydroquinone was in excess; whereas in the second case, quinone was always in excess.* Hence he concludes that the true formula of quinhydrone is $C_{12}H_{10}O_4$; and that other quinhydrones must, similarly, be composed of quinone and hydroquinone in equal numbers of molecules.
J. R.

Formula of Quinhydrone. By H. WICHELHAUS (*Deut. Chem. Ges. Ber.*, 1781—1783).—The author defends the empirical formula, $C_{18}H_{14}O_6$, assigned by him to quinhydrone, against the strictures of Liebermann, and further shows that his hypothesis of the constitution of this body, out of 1 mol. quinone and 2 mols. hydroquinone, is not inconsistent with its formation by the reaction of its constituents in the proportion of single molecules. For, in the formation of 1 mol. quinhydrone from a mixture of 2 mols. quinone and 2 mols. hydroquinone, 1 mol. hydrogen is liberated, and 1 mol. quinone remains. Of these the former is sufficient to convert the latter into hydroquinone. Since this action occurs gradually, and the resulting formation of hydroquinone determines a further production of quinhydrone, it is not unreasonable to suppose that when $\frac{2}{3}$ of the quinone have been reduced to hydroquinone, the remaining $\frac{1}{3}$ will have disappeared, the whole having united to form quinhydrone. C. F. C.

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* Quinone, in aqueous solution, may be readily detected by means of an alcoholic solution of hydrocœrulignone, one drop of which added to a quinone solution instantly colours it yellowish-red, and then causes a deposit of the steel-blue iridescent needles of cœrulignone. The reaction is exceedingly delicate: it depends upon the conversion of hydrocœrulignone into cœrulignone on the one hand, and of quinone into hydroquinone on the other. Hydrocœrulignone may likewise be employed for the detection of many oxidizing agents.—J. R.

Constitution of the Catechins. By A. GAUTIER (*Compt. rend.*, lxxxv, 752—755).—When the catechins obtained from acacia catechu, (which the author has shown to have the formula, $C_{21}H_{18}O_8$, and not $C_{19}H_{18}O_4$, which Hlasiwetz assigned to them), are treated with potash, they yield protocatechuic acid, phloroglucin, and formic acid, which in some cases is decomposed into marsh gas and carbon dioxide. When they are treated with hydriodic acid, iodoform is found amongst the products of decomposition. From these reactions it appears that these catechins contain either the group, $—CH_2—CH\equiv C\equiv O_2$, or the group, $—CH_2—CO—CHO$.

The action of sulphuric acid gives rise to protocatechuic acid, a phenol having the formula, $C_{14}H_{16}O_7$, and an anhydride of the latter, $C_{28}H_{22}O_7$. Owing to some error in the structural formulæ given in the paper, it is impossible to reproduce them. L. T. O'S.

Parabromobenzyl Compounds. By C. L. JACKSON and W. LOWERY (*Deut. Chem. Ges. Ber.*, x, 1209—1212).—*Parabromobenzyl alcohol*, $C_6H_4Br.CH_2OH$, is most easily prepared by boiling parabromobenzyl bromide with water for some days, in a flask with reversed condenser. It is also obtained by heating parabromobenzyl acetate to 150° with aqueous ammonia. It forms long, colourless, elastic, flat needles, having a fine nacreous lustre and unpleasant odour, melting at 69°, and dissolving easily in boiling water, alcohol, ether, benzene, and carbon bisulphide.

The *acetate*, formed by heating the bromide with sodium acetate in alcohol, decomposes when distilled, and has not yet been obtained pure.

The *cyanide*, $C_6H_4Br.CH_2CN$, is obtained by boiling the bromide with alcoholic solution of potassium cyanide. It is a crystalline body of strong disagreeable odour, melting at 46°, and dissolving easily in alcohol, ether, benzene, glacial acetic acid, and carbon bisulphide, but not in water.

The *thiocyanate*, $C_6H_4Br.CH_2SCN$, formed by boiling the bromide with potassium thiocyanate, crystallises in needles, melting at 25°, and dissolving very easily in alcohol.

Parabromalphatoluic acid, $C_6H_4Br.CH_2.COOH$, formed by heating the above cyanide to 100°, with hydrochloric acid in sealed tubes, crystallises in long white needles, which melt at 114·5°. It decomposes carbonates very slowly, but dissolves readily in ammonia and soda-ley, forming salts. By oxidation with chromic acid it is converted into parabromobenzoic acid. The ammonium, silver, copper, calcium, and barium salts have been prepared. The ammonium salt forms precipitates with mercuric, mercurous, ferrous, and lead salts, but not with salts of aluminium, chromium, zinc, cobalt, nickel, or magnesium.

Parabromobenzyl bromide reacts with alcoholic ammonia at the ordinary temperature, to form *triparabromobenzylamine*, $(C_6H_4BrCH_2)_3N$, and the corresponding *hydrobromide*, $(C_6H_4BrCH_2)_3NHBr$. The former crystallises from alcohol in needles, which melt at 78—79°; the latter is deposited from the alcoholic liquid in which it is formed in white, nacreous scales, melting at 270°, insoluble in water and alcohol, but easily soluble in ether. J. R.

A Nitrobenzaldehyde analogous to the Nitrobenzoic Acid melting at 127°.—By F. FITTICA (*Deut. Chem. Ges. Ber.*, x, 1630—1633).—This substance is formed, together with a large quantity of the ordinary crystalline modification, on dropping a mixture of equal weights of ordinary benzaldehyde and ethyl nitrate into strong sulphuric acid, maintained at the temperature of 30—35°. It is an oily body, having the characteristic properties of the aldehydes. By oxidation with chromic acid it yields an acid melting at 127°, and having the other characters of the fourth nitrobenzoic acid.

J. R.

Derivatives of Paraoxybenzaldehyde. By HERMANN HERZFELD (*Deut. Chem. Ges. Ber.*, x, 1267—1272).—This is a continuation of a previous paper by the author and Tiemann (*Deut. Chem. Ges. Ber.*, x, 63).

Paraoxybenzylalcohol, $C_6H_4(OH)CH_2OH$, is formed by the action of sodium-amalgam on paraoxybenzaldehyde. It is a solid crystalline substance, melting at 197·5°, soluble in water, alcohol, and ether, and sparingly in benzene and chloroform. It gives a transient blue coloration with ferric chloride, and is coloured brown by strong sulphuric acid.

Hydroparaoxybenzoïn, $C_{14}H_{14}O_4$, is produced on treating with sodium-amalgam a mixture of paraoxybenzaldehyde with more than 10 parts of water. It is thrown down, on neutralising the liquid, as a white crystalline substance, melting at 222°, easily soluble in boiling water less easily in alcohol, benzene, and chloroform.

Nitroparaoxybenzaldehyde, $C_6H_3OH(NO_2)COH$, is formed by dropping strong nitric acid into a mixture of 3 parts of paraoxybenzaldehyde with 20 parts of strong sulphuric acid. On diluting with water it is deposited as a golden-yellow mass, which crystallises in yellow needles from its aqueous solution. It melts at 139—140°, dissolves easily in alcohol and benzene, sparingly in ether and chloroform, sublimes entirely on heating, and volatilises with steam. It forms a crystalline, sparingly soluble compound with acid sodium sulphite, and produces a transient reddish coloration with ferric chloride.

Paraoxybenzaldehyde absorbs 13·46 per cent. (= 1 mol.) of dry ammonia gas, forming with it an oily body, which, on exposure to air, gradually gives off ammonia, and leaves unaltered aldehyde.

Salicylic aldehyde likewise absorbs 1 mol. of ammonia, forming a compound which is resolved by heat into water, ammonia, and hydrosalicylamide.

Paraoxybenzaldehyde in ethereal solution reacts with aniline to form a pale-yellow crystalline body, which melts at 190—191°, and dissolves easily in alcohol and ether, sparingly in benzene and chloroform. From the analysis of the body it appears to be formed by the following reaction:—

$$C_7H_6O_2 + C_6H_7N = C_{13}H_{11}NO + H_2O.$$

J. R.

Aldehyde Compounds. By E. HEPP (*Deut. Chem. Ges. Ber.*, x, 1649—1652).—The author showed in a former paper (*Deut. Chem. Ges. Ber.*, ix, 1424) that benzonitril reacts with the normal aldehydes of the fatty series to form compounds in which the oxygen of the aldehydes is replaced by two benzamide residues, $NH.COC_6H_5$. In the present paper he describes other bodies of analogous constitution.

Methylene-diphenylacetamide is formed by heating a mixture of 1 mol. of methylal and 2 mols. of benzyl cyanide with concentrated sulphuric acid. It crystallises in small, white needles, which melt at 205°, and distil for the most part without decomposition. It is nearly insoluble in water and ether, but soluble in carbon bisulphide, boiling alcohol and glacial acetic acid. Its composition and reactions show that its formula is $CH_2(NH.CO.CH_2.C_6H_5)_2$. When heated with hydrochloric acid or alcoholic potash in sealed tubes, it yields phenylacetic acid. By oxidation with manganese dioxide and dilute sulphuric acid, it yields phenylacetamide in theoretical proportion.

Trichlorethylidene-diphenylacetamide is obtained from benzyl cyanide and chloral in the same manner as the preceding compound. It forms small white needles, which sublime without melting. Its composition agrees with the formula, $CCl_3.CH(NH.CO.CH_2.C_6H_5)_2$.

Trichlorethylidene-diacetamide, $C_6H_9Cl_3O_2N_2$, is obtained by simply heating to 40—50° a mixture of acetonitril and chloral. It forms silky needles, which sublime without decomposition before melting.

J. R.

Phthalic Acid. By JULIUS HESSERT (*Deut. Chem. Ges. Ber.*, x, 1445).—The author, in continuation of Baeyer's work on this subject, finds that the best method for preparing the above compound is by the action of zinc and hydrochloric acid on an ethereal solution of phthalyl chloride. In this manner 4 to 5 grams of the aldehyde were obtained from 10 to 12 grams of the chloride.

The melting point of phthalyl aldehyde is 67° according to Kolbe and Wischin; the author, however, finds that its melting point is 73°. By the action of alkalis or their carbonates phthalyl aldehyde is converted into a new acid thus: $C_6H_4(COH)_2 + H_2O = C_6H_4(COOH)(CH_2.COH)$. This acid is much less soluble in cold water than the aldehyde, but dissolves easily in alcohol and ether. It melts at 118°, giving up one molecule of water, and being reconverted into the original aldehyde, the same reaction takes place on boiling with water. The barium, silver and lead salts were prepared. The acid is monobasic, and bears the same relation to phthalic acid as glycollic does to oxalic.

Sodium-amalgam only partly reduces a solution of phthalic aldehyde in dilute alcohol, the greater part of the aldehyde forming with the alkali the sodium-salt of the above-mentioned acid, which is not further attacked by the amalgam; by keeping the liquid acid, however, the reduction is complete, and phthalyl pinacone,

$$(CH_2.OH—C_6H_4—CHOH)_2,$$

is produced, which, when treated with potassium permanganate, yields an acid having the properties and composition of the diphthalic acid described by Ador, thus:

$$CH_2.OH—C_6H_4—CHOH)_2 + 3O_2 = (COOH—C_6H_4.CO)_2 + 4H_2O.$$

Phthalic acid is also simultaneously produced, owing to the further action of the oxidising agent on the diphthalic acid.

Phthalyl pinacone crystallises in needles (m.p. =197°). It is soluble in water and alcohol, difficulty soluble in ether and insoluble in chloroform. By the action of sodium-amalgam on phthalyl aldehyde there is also formed, in addition to the pinacone, the aldehyde-alcohol of phthalic acid, $CH_2.OH—C_6H_4—COH$, which by oxidation is converted into phthalic acid.

Ammonia and ammonium sulphide have no action on the alcoholic or ethereal solution of phthalyl aldehyde even at 220°, but at 240° a crystalline substance is obtained, which is insoluble in water, alcohol, ether, and carbon disulphide, but soluble in boiling glacial acetic acid, crystallizing therefrom on cooling in stellate groups of needles, which do not melt at 260°. The analysis of this body is not yet completed. By heating phthalyl aldehyde with aniline to 200—220°, the aniline compound, $COH—C_6H_4—CH.NC_6H_5$, is formed, which melts at 160°, and crystallizes in small plates, which dissolve with difficulty in boiling water and ether, but easily in benzol and chloroform. The author is continuing his investigation. T. C.

Paratolylphenyl Ketone. By W. Thörner (*Liebig's Annalen*, clxxxix, 83—128). This compound is best prepared by the method of Collarits and Merz (*Deut. Chem. Ges. Ber.*, vi, 537), an intimate mixture of three parts of benzoic acid, four of toluene, and the same quantity of phosphorus pentoxide and of sand being heated for eight to ten hours to 200—220°. By this process 1,000 grams of benzoic acid yielded 330° pure paratolyphenyl ketone, and 402° of the liquid ortho-compound still containing some of the solid. When the para-compound is heated with phosphorus pentachloride, it appears to be converted into the ketonic dichloride, which, however, could not be isolated, as it decomposes on distillation. Dry chlorine acting on the heated ketone replaces the hydrogen in the methyl-group, and by regulating the temperature and the quantity of chlorine, the three chlorides can easily be obtained pure.

Parabenzoylbenzyl chloride, $C_6H_5.CO.C_6H_4.CH_2Cl$, is formed at 100—

110°, and purified by crystallisation from alcohol and washing with ether, which removes some dichloride. It forms long white prisms melting at 97—98°. On adding a little water to its solution in absolute alcohol it crystallises in long, slender, silky needles. It is readily soluble in chloroform, carbon sulphide, benzene, toluene, hot alcohol, and glacial acetic acid, more sparingly in cold alcohol and ether. It can be sublimed, and easily undergoes double decompositions.

Parabenzoylbenzylene dichloride, $C_6H_5.CO.C_6H_4.CHCl_2$, is produced by the continued action of chlorine at 130—140°, and crystallises from alcohol and acetic acid in silky plates, melting at 94—95°. It dissolves easily in the same solvents as the monochloride, and also in ether. It can be sublimed, and boiling alkalis convert it slowly into parabenzoylbenzoic acid. When it is heated with alcohol and silver nitrate, or with water and silver oxide or lead oxide, the same acid is formed, and not the aldehyde.

Parabenzoylbenzenyl trichloride, $C_6H_5.CO.C_6H_4.CCl_3$, is formed at 150—160°; like the preceding compound, it is best purified by the fractional precipitation of its boiling solution in glacial acetic acid with water. It crystallises in small glistening plates or larger thin square plates, melting at 111—111·5°. It does not dissolve very freely in cold alcohol and acetic acid, but readily in the hot liquids and in the solvents mentioned above. It can be sublimed, and on heating it with water or silver nitrate to 170—180°, or boiling it with alkalis, it is converted into parabenzoylbenzoic acid. On heating it with phosphorus pentachloride, it is converted into $C_3H_5.CCl_2.C_6H_4.CCl_3$, which is readily soluble in acetic acid, carbon sulphide, benzene, &c. It crystallises in square striated thin plates, melting at 78—80°; it cannot be sublimed, and is converted in parabenzoylbenzoic acid by concentrated nitric acid, and by boiling it with alkalis.

To convert the ketone into the secondary alcohol or the pinacone, its alcoholic solution was treated with sodium or its amalgam, but without effect; whereas on using zinc and hydrochloric acid, two isomeric *pinacolins*, $C_{28}H_{24}O$ were formed.

The *α-pinacolin*, which is the first product, is easily converted into the β-compound, and therefore obtained pure only by working under certain conditions. A good yield is obtained by dissolving 10 grams of the ketone in 500 c.c. of alcohol of 75 per cent., and adding to it a mixture of zinc and so much hydrochloric acid that a brisk evolution of hydrogen goes on in the cold. It is then boiled for two or three hours, and the pinacolin which has separated out is purified by crystallising it from alcohol. It forms microscopic glistening needles, melting at 214—215°, and dissolves freely in chloroform, carbon sulphide, toluene, and boiling acetic acid, less readily in boiling alcohol and ether, very sparingly in cold alcohol.

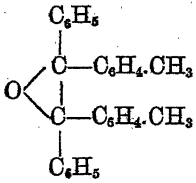
The *β-pinacolin* is much more easily obtained by using a stronger alcoholic solution of the ketone, and allowing the reaction to go on for four or five days. It crystallises from hot absolute alcohol in very refractive, small square plates, which become opaque on drying, and turn yellow on exposure to light. It readily dissolves in the same liquids as the α-compound, and also in boiling alcohol. When the α-pinacolin is heated with benzoyl chloride or with concentrated hydrochloric acid to 150—160°, or with glacial acetic acid to 170—180°, it is converted into the β-compound. The α-compound is scarcely acted upon by boiling with nitric acid, an aqueous solution of chromic acid, or potassium permanganate, but a boiling solution of chromic trioxide in acetic acid oxidises it again to paratolyphenyl ketone.

The β-pinacolin cannot be converted into the α-compound; on heating it or the latter with concentrated hydriodic acid and amorphous phosphorus to 210—220°, the hydrocarbon, $C_{28}H_{26}$, is formed, which is readily soluble in chloroform, carbon sulphide, and toluene, but very sparingly in cold alcohol and ether. It separates from boiling alcohol or acetic acid in microscopic, probably triclinic crystals, melting at 213—213·5°.

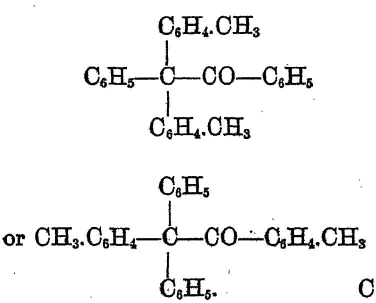
On boiling the β-pinacolin with glacial acetic acid and chromic trioxide, a large portion is completely burnt to carbon dioxide, and only a small quantity of an acid is obtained having the formula $C_{21}H_{18}O_2$, or more probably $C_{22}H_{20}O_2$, some benzoic acid being formed at the same time. The new acid separates from ether as an amorphous transparent mass, and is precipitated from an ammoniacal solution by hydrochloric acid, as a bulky amorphous white powder. It dissolves freely in ether, benzene, alcohol, glacial acetic acid, &c., melts at 78—83°, and cannot be sublimed. Its alkaline solution is precipitated by carbon dioxide; the salts which it forms with the alkali-metals are amorphous and deliquescent, the other salts are gelatinous precipitates.

From the results of this paper it appears most probable that, by the action of nascent hydrogen on the ketone, first the corresponding pinacone is produced, which, however, at once loses the elements of water and is converted into the α-pinacolin. As this compound can be easily reconverted into the ketone, it must have a similar constitution, while the β-compound, which by oxidation loses carbon and yields a monobasic acid, is produced by an intramolecular change, and its constitution will therefore be similar to that of the common pinacolin from acetone, which by oxidation yields trimethyl-acetic acid.

α-pinacolin.



β-pinacolin.



$$C_6H_5-\overset{C_6H_4.CH_3}{\underset{C_6H_4.CH_3}{C}}-CO-C_6H_5$$

$$\text{or } CH_3.C_6H_4-\overset{C_6H_5}{\underset{C_6H_5.}{C}}-CO-C_6H_4.CH_3$$

C. S.

Synthesis of Benzoic Acid and Benzophenone. By Friedel, Crafts, and Ador (*Compt. rend.*, lxxxv, 673—676). When carbonyl chloride acts on benzene in presence of aluminium chloride, the final product of the reaction is benzophenone, and under certain conditions benzoic acid is formed. The reaction is expressed as follows:—first, benzoyl chloride is formed ($C_6H_6 + COCl_2 = C_6H_8COCl + HCl$), which acts on another molecule of benzene, forming benzophenone—

$$C_6H_8COCl + C_6H_6 = C_6H_5.CO.C_6H_5 + HCl.$$

Toluene and xylene behave in a similar manner. L. T. O'S.

Three Isomeric Bromamidophenylacetic Acids. By P. P. BEDSON (*Deut. Chem. Ges. Ber.*, x, 1657—1659). This is a continuation of a previous paper on derivatives of phenylacetic acid (*Deut. Chem. Ges. Ber.*, x, 530).

Parabromo-metanitro-phenylacetic acid yields, by reduction with tin and hydrochloric acid, a crystalline compound of stannous chloride with the hydrochloride of bromamidophenylacetic acid. On treating the compound with hydrogen sulphide, the latter constituent is obtained in white needles agreeing in composition with the formula, $C_7H_7BrN.CO_2H.HCl + H_2O$; and from this salt, by further treatment with ammonia and acetic acid, *parabromometamido-phenylacetic acid*, $C_6H_3.BrNH_2.CH_2COOH$, is obtained in white silky needles, which dissolve in hot water, alcohol, and chloroform, and slowly turn red in the air.

Parabromo-orthonitro-phenylacetic acid yields by the same treatment a bromamidophenylacetic acid isomeric with the foregoing crystallising in white flat needles, which speedily turn red in the air and melt at 167°.

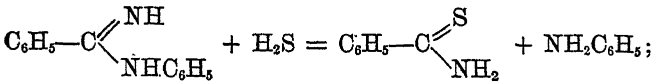
A third isomeride, melting at 186°, is still under investigation.

J. R.

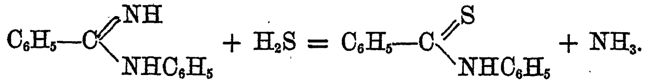
Action of Bromine on Ethylphthalimide. By A. MICHAEL (*Deut. Chem. Ges. Ber.*, x, 1644).—Ethylphthalimide, obtained by distilling a solution of phthalic anhydride in aqueous ethylamine, crystallises in long white needles, melting at 78—79°. When heated to 130—140° with excess of bromine, it yields *tribromethylphthalimide*. This substance crystallises in truncated prisms, melts with decomposition at 186—189°, and dissolves in hot alcohol but not in water. It is decomposed by boiling with potash. J. R.

Thiamides of Monobasic Organic Acids. By AUGUST BERNTHSEN (*Deut. Chem. Ges. Ber.*, x, 1238—1242).—It has been shown by the author (*Liebig's Annalen*, clxxxiv, 290) that thiamides when treated with the hydrochlorides of primary amines, are converted into amidines, with elimination of hydrogen sulphide. Conversely, he now finds that amidines, when treated with hydrogen sulphide, yield thiamides.

When hydrogen sulphide is passed over fused benzenylmonophenylamidine, at 130°, a reaction takes place which results in the evolution of ammonia and aniline, and the production of *benzothiamide* and *benzothianilide*. The formation of these bodies is due to two simultaneous decompositions, represented thus:—

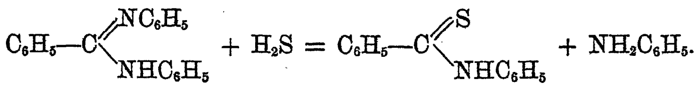


$$C_6H_5{-}C\left\langle\begin{matrix}NH\\NHC_6H_5\end{matrix}\right. + H_2S = C_6H_5{-}C\left\langle\begin{matrix}S\\NH_2\end{matrix}\right. + NH_2C_6H_5;$$



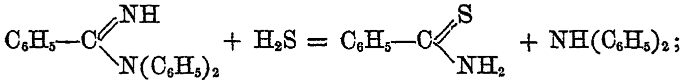
$$C_6H_5{-}C\left\langle\begin{matrix}NH\\NHC_6H_5\end{matrix}\right. + H_2S = C_6H_5{-}C\left\langle\begin{matrix}S\\NHC_6H_5\end{matrix}\right. + NH_3.$$

Benzenyldiphenylamidine, submitted to the action of hydrogen sulphide, at 166°, yields benzothianilide and aniline—

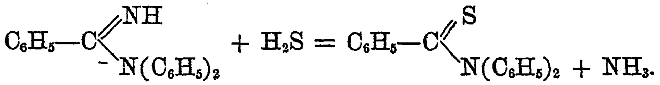


$$C_6H_5{-}C\left\langle\begin{matrix}NC_6H_5\\NHC_6H_5\end{matrix}\right. + H_2S = C_6H_5{-}C\left\langle\begin{matrix}S\\NHC_6H_5\end{matrix}\right. + NH_2C_6H_5.$$

Benzenylisodiphenylamidine, similarly treated, gives off ammonia and yields diphenylamine, benzothiamide, and a new compound which crystallises in small golden-yellow crystals, soluble in hot alcohol, ether, and benzene. This last appears to be *benzodiphenylthiamide.* The reactions are thus expressed:—

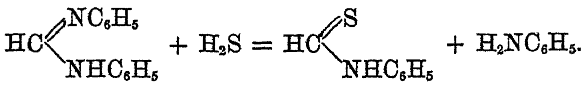


$$C_6H_5{-}C\left\langle\begin{matrix}NH\\N(C_6H_5)_2\end{matrix}\right. + H_2S = C_6H_5{-}C\left\langle\begin{matrix}S\\NH_2\end{matrix}\right. + NH(C_6H_5)_2;$$



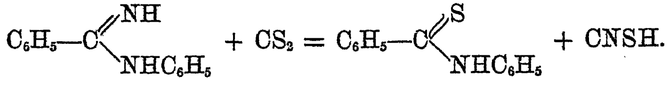
$$C_6H_5{-}C\left\langle\begin{matrix}NH\\N(C_6H_5)_2\end{matrix}\right. + H_2S = C_6H_5{-}C\left\langle\begin{matrix}S\\N(C_6H_5)_2\end{matrix}\right. + NH_3.$$

Similarly, methenyldiphenylamidine, exposed to the action of hydrogen sulphide at 140—150°, yields aniline and *formothianilide*, a body identical with that which Hofmann obtained (*Deut. Chem. Ges. Ber.*, x, 1095) by the action of hydrogen sulphide on phenyl isocyanide—



$$HC\left\langle\begin{matrix}NC_6H_5\\NHC_6H_5\end{matrix}\right. + H_2S = HC\left\langle\begin{matrix}S\\NHC_6H_5\end{matrix}\right. + H_2NC_6H_5.$$

The analogy of the thiamides of monobasic acids to thiocarbamides is shown by the fact that carbon bisulphide acts upon benzenylphenylamidine at 100—120° to form thiocyanic acid and benzothianilide—



$$C_6H_5{-}C\left\langle\begin{matrix}NH\\NHC_6H_5\end{matrix}\right. + CS_2 = C_6H_5{-}C\left\langle\begin{matrix}S\\NHC_6H_5\end{matrix}\right. + CNSH.$$

J. R.

Contributions to the Knowledge of the Three Isomeric Oxybenzoic Acids. By H. SMITH (*J. pr. Chem.* [2], xvi, 218—233).—Salicylic acid, and paraoxybenzoic acid, when treated with dry ammonia, give first the ammonium salts, which on heating yield phenol and carbonic acid.

Oxybenzoic acid, however, when similarly treated, yields oxybenzonitril, according to the equation—

$$C_6H_4\left\{\begin{matrix}OH\\CO.ONH_4\end{matrix}\right. + NH_3 = C_6H_4\left\{\begin{matrix}OH\\CN\end{matrix}\right. + 2H_2O + NH_3.$$

This oxybenzonitril melting at 82°, corresponds with that prepared by Griess from the sulphate of diazocyanbenzene, $C_6H_3(CN)N_2H_2SO_4$ (*Deut. Chem. Ges. Ber.*, v, 669).

The three isomeric acids show a similar behaviour when distilled with potassium thiocyanate, the oxybenzoic acid alone yielding the nitril. This method of preparing the nitril is, however, less to be recommended than the former.

The oxybenzonitril yields, by treatment with sulphuric acid and nitric acid, a mononitrated substitution-compound melting at 182—183°, which on boiling with alkalis yields a nitro-oxybenzoic acid.

The sulpho-oxybenzonitril has not been prepared in the pure state.

P. P. B.

Double salts of Two Organic Acids. By H. SALKOWSKI (*Deut. Chem. Ges. Ber.*, x, 1257—1259).—The author described in a previous paper a barium double salt of benzoic and paranitrobenzoic acids (*Deut. Chem. Ges. Ber.*, ix, 24; abstr. *Journ. Chem. Soc.*, 1876, i, 710). He has now succeeded in isolating *strontium* and *calcium* double salts of the same acids. The salts were obtained by neutralising a mixture of the two acids in molecular proportions with strontium or calcium carbonate, and allowing saturated aqueous solutions to evaporate spontaneously in the air. Their composition is expressed by the formulæ—

$$C_6H_4(NO_2)CO_2.Sr.CO_2.C_6H_5 + H_2O \text{ and } C_6H_4(NO_2)CO_2.Ca.CO_2.C_6H_5 + 3H_2O.$$

A *calcium* double-salt of *benzoic* and *metanitrobenzoic acids* has also been obtained in the same manner; but it was not found possible to prepare the corresponding strontium and barium double salts, owing, apparently, to the great difference in solubility of the benzoates and metanitrobenzoates of these bases.

J. R.

Constitution of Dinitro-anisic Acid and its Derivatives. By H. SALKOWSKI and C. RUDOLPH (*Deut. Chem. Ges. Ber.*, x, 1254—1257).—This acid is obtained by the action of a cooled mixture of concentrated nitric and sulphuric acids on nitro-anisic acid. It crystallises in delicate needles, which melt at 181—182°.

Dinitro-anisic acid is converted, by heating to 150° with water, into dinitroparaoxybenzoic acid, in accordance with the equation—

$$C_6H_2(NO_2)_2OCH_3.CO_2H + H_2O = C_6H_2(NO_2)_2OH.CO_2H + CH_3OH.$$

On more prolonged heating to 170°, however, the dinitroparaoxybenzoic acid disappears, and β-dinitrophenol is formed.

Now, since anisic acid belongs to the para-series, and since, moreover, both nitro-groups in β-dinitrophenol occupy positions contiguous to the hydroxyl-group, it is obvious that the constitution of the following compounds must be expressed by the accompanying formulæ :—

Dinitro-anisic acid $(C_6H_2)OCH_3 : NO_2 : CO_2H : NO_2 = 1 : 2 \quad 4 : 6$;
Dinitroparaoxybenzoic acid .... $(C_6H_2)OH : NO_2 : CO_2H : NO_2 = 1 : 2 : 4 : 6$;
Dinitroparamidobenzoic acid .... $(C_6H_2)NH_2 : NO_2 : CO_2H : NO_2 = 1 : 2 : 4 : 6$.

Mononitro-anisic acid, when heated to 220° with water, is converted into a carbonaceous mass containing orthonitrophenol, but no nitroparaoxybenzoic acid, the latter substance being probably decomposed at the high temperature:—

$$C_6H_3.NO_2.OCH_3.CO_2H + H_2O = C_6H_4.NO_2.OH + CH_3.OH + CO_2.$$

J. R.

Oxyterephthalic Acid. By G. A. BURKHARDT (*Deut. Chem. Ges. Ber.*, x, 1273).—This acid, when treated with a mixture of fuming nitric and Nordhausen sulphuric acids, yields *dinitro-oxyterephthalic acid*, which crystallises from cold water in fine golden-yellow transparent crystals, dissolving easily in cold water and melting at 178°. No isomeric acid is formed. The dinitro-acid and its salts are explosive.

The *acid silver salt*, $C_6H(NO_2)_2OH(COOH)COOAg$, formed on mixing concentrated solutions of the acid and of silver nitrate, is a yellow crystalline powder, moderately soluble in water.

The *neutral silver salt*, $C_6H(NO_2)_2OH(COOAg)_2$, is obtained by triturating a concentrated solution of the acid with moist silver oxide, and evaporating the filtrate over sulphuric acid. It forms blood-red prismatic crystals, very easily soluble in water. It crystallises from aqueous solution with 2 mols. of water.

The *acid lead salt*, $C_6H(NO_2)_2OH(COOH)COOpb$ ($pb = 103{\cdot}5$), formed on adding neutral lead acetate to a solution of the acid, is a yellow crystalline powder, sparingly soluble in water.

The *neutral calcium salt*, $C_6H(NO_2)_2OH(COO)_2Ca$, formed by boiling a solution of the acid with calcium carbonate, is yellow and crystalline, and dissolves sparingly in water. J. R.

Action of Sodium Amalgam on α-Nitronaphthalenesulphonic Acid. By CLAUS and GRAEFF (*Deut. Chem. Ges. Ber.*, x, 1303).—Hoping that bodies analogous to the azobenzoic acid and azophenylene producible from nitrobenzenesulphonic acid would be obtained from α-nitronaphthalenesulphonic acid, the author subjected this acid to the action of sodium amalgam; but whether the solution were acid or alkaline, the same result followed, viz., splitting up into naphthylamine and sulphuric acid without the formation of any azonaphthalenesulphonic acid. On the other hand, the nitrobenzenesulphonic acid obtained by acting with fuming sulphuric acid on nitrobenzene is readily and completely converted into azobenzenesulphonic acid by sodium amalgam, no aniline or sulphuric acid being formed. The authors hence conclude that naphthalene has a different structure from true aromatic bodies, being presumably unsymmetrical.

C. R. A. W.

Isomeric Sulpho- and Oxynaphthoic Acids. By M. STUMPF (*Liebig's Annalen*, clxxxviii, 1—13). By dissolving napthoic acid in warm fuming sulphuric acid three isomeric sulphonic acids are formed, which are distinguished as α, β, and γ. The first of these has already been described by Battershall (*Liebig's Annalen*, clxviii, 114). To separate the acids, they are converted into the barium salts; on concentrating the solution first a small quantity of the impure salt of the β-acid separates in hard nodular crystals, and then a large quantity of the α-sulphonate, forming hard, glistening monoclinic crystals, which by recrystallisation are easily obtained pure. The salts contained in the mother-liquors are then converted into the acid salts, of which that of the γ-acid is but sparingly soluble, while those of the β-acid and α-acid, which remain in the mother-liquor, can be separated only by repeated crystallisations.

On fusing the acids with potash they yield three isomeric oxynaphthoic acids, which when heated with lime are easily resolved into carbon dioxide and naphthols.

α-Sulphonaphthoic acid, $C_{10}H_6(SO_3H)CO_2H$, is readily soluble but not deliquescent, and crystallises in prisms, melting without decomposition at 235°.

The acid salt $(C_{11}H_7SO_5)_2Ba + 2H_2O$, which was prepared to compare it with its isomerides, is more soluble than the normal salt, and crystallises in glistening prisms.

α-Oxynaphthoic acid, $C_{10}H_6(OH)SO_3H$, has also been obtained by Battershall; it crystallises from boiling water in thin needles, melting at 234—237°, and when distilled with lime yields α-naphthol.

β-Sulphonaphthoic acid forms a crystalline mass, and is more freely soluble than the α-acid; it melts and decomposes at 218—222°. $C_{11}H_6SO_5Ba + 3\frac{1}{2}H_2O_5$ crystallises in tufts of thick glistening needles, which are a little more soluble than the normal α-salt. $(C_{11}H_7SO_5)_2Ba = 4H_2O$ is more freely soluble, and forms soft, voluminous, warty masses. $C_{11}H_6SO_5K_2$ is a white, crystalline, deliquescent mass.

β-Oxynaphthoic acid crystallises from boiling water in bulky masses, consisting of fine needles and from alcohol in druses, which are lined with fine hairs. It melts, but not without decomposition, at 245—247°. On heating it with lime it yields β-naphthol.

γ-Sulphonaphthoic acid is freely soluble in water, and crystallises in small matted needles, melting at 182—185°, and decomposing at 187°.

$C_{11}H_6S_2O_5Ba + 1\frac{1}{2}H_2O$ is tolerably soluble in water, and does not crystallise well. $(C_{11}H_7S_2O_5)_2Ba + H_2O$ is so sparingly soluble, that a solution of the free acid is precipitated by barium chloride, and one of the normal salt by hydrochloric acid. From boiling water, in which it dissolves also sparingly, it crystallises in small, hard, warty masses. $C_{11}H_6SO_5K_2$ is a crystalline, deliquescent mass, and crystallises from boiling absolute alcohol in tufts of needles.

γ-Oxynaphthoic acid is sparingly soluble in cold water, more readily in hot water, very freely in alcohol, and crystallises in ramified needles melting at 186—187° without decomposition. It has some resemblance to Eller and Schäffer's carbonaphtholic acid, which is formed by the action of sodium and carbon dioxide on α-naphthol. Both

acids however differ, not only by their reactions and salts, but also by their decomposition with lime, the γ-acid yielding β-naphthol.

When isonaphthoic (β-naphthoic) acid is dissolved in fuming sulpuric acid, *sulphisonapthoic* acid is formed, which has also already been obtained by Battershall. It is a white crystalline mass, which dissolves readily in water, and melts at 229—230°. Besides this acid a minute quantity of an isomeride is formed.

$C_{11}H_6SO_6Ba + 6H_2O$ crystallises in tufts of long, silky needles; Battershall obtained it in monoclinic or triclinic crystals, with only one molecule of water. $(C_{11}H_7SO_5)_2Ba + 6\frac{1}{2}H_2O$ forms long silky needles, or small plates. $C_{11}H_6SO_5K_2$ is readily soluble, and crystallises from water in small needles, and from alcohol in slender, silky prisms.

Oxyisonaphthoic acid crystallises from alcohol in tufts of glistening needles, melting at 210—211°. On distilling with lime, α-napthol is obtained.

The following table explains itself:—

	Melting-point.	Position.		Crystallisation from		Precipitate with ferric chloride.
		CH.	CO_2H.	Water.	Alcohol.	
α-Oxynaphthoic acid..	234—237°	α.	α.	Needles	—	Dirty violet.
β-Oxynaphthoic acid..	245—247°	β.	α.	Needles	Druses	Reddish brown on heating.
γ-Oxynaphthoic acid..	186—187°	β.	α.	Needles	—	Chocolate.
α-Carbonaphtholic acid	185—186°	α.	?	Needles	Needles	Deep blue colour, no precipitate.
α-Oxyisonaphthoic acid	210—211°	α.	β.	Needles	Needles	Dirty crimson.
β-Carbonaphtholic acid	?	β.	?	?	?	Deep, blackish violet.

C. S.

Haloïd Derivatives of Anthracene and Phenanthrene. By V. MERZ and W. WEITH (*Deut. Chem. Ges. Ber.*, x, 1233).—The most highly chlorinated derivatives of anthracene, anthraquinone, and alizarin, formed by the action of antimony perchloride, are respectively octo-, penta-, and tetra-chlorocompounds. Further action of the reagent results in the breaking up of these products, with formation of perchlorobenzene and perchloromethane, the anthraquinone-derivative yielding also carbon dioxide, and the alizarin-derivative, perchlorethane.

Bromine acting on the same substances produces ultimately *octobromanthracene*, *pentabromanthraquinone*, and *tetrabromalizarin*. Of these products, the first two are not further affected by bromine containing iodine, but the last breaks up below 200° into pentabromobenzene, carbon dioxide, and perbromethane.

Tribromanthraquinone, when fused with soda or potash, yields purpurin, and at higher temperatures with potash an oxypurpurin.

The ultimate products of the action of chlorine and bromine on phenanthrene are *octochloro-*, and *pentabromo-phenanthrene.* The former is easily resolved on heating into perchlorobenzene and perchloromethane.

Diphenol, carbazol, and benzidine, when treated with chlorine, yield simply *perchlorodiphenyl.*

Chrysene heated with antimony perchloride yields much perchlorobenzene, together with perchlorinated ethane and methane.

Perbromophenol, formed by the action of bromine containing iodine on phenol, is converted into perbromobenzene by heating with phosphorus pentabromide. J. R.

Brominated Derivatives of Anthracene. By W. HAMMERSCHLAG (*Deut. Chem. Ges. Ber.*, x, 1212—1214).—Tetrabromanthracene, exposed to the vapour of bromine for some days, is converted into *tetrabromanthracene tetrabromide*, $C_{14}H_6Br_8$, which crystallises from a hot saturated solution in carbon bisulphide in distinct, colourless prisms melting, with decomposition, about 212°.

The tetrabromide, heated to 230° till it ceases to give off bromine and hydrogen bromide, yields *pentabromanthracene.* This is a pulverulent yellow substance, melting about 212°, and dissolving sparingly in alcohol and ether, but easily in benzene, toluene, and carbon bisulphide. By oxidation with chromic acid it is converted into *tetrabromanthraquinone*, a body subliming in broad needles, which melt at 365°.

The tetrabromide reacts violently with alcoholic soda when warmed therewith, yielding *hexbromanthracene*, a substance which dissolves but sparingly in any solvent, and crystallises from naphtha in yellow silky needles, infusible at 370°.

Hexbromanthrene is completely converted into *tetrabromanthraquinone* by oxidation with acetic and chromic acids. This is only slightly soluble in all liquids, and is deposited from solution in the form of powder. By sublimation it may be obtained in thin needles or laminæ, infusible at 370°.

Tetrabromanthraquinone, when fused with sodium hydrate, yields alizarin and a small quantity of a colourless product not yet examined.

J. R.

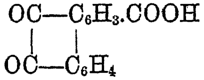
Phenanthrol. By G. REHS (*Deut. Chem. Ges. Ber.*, x, 1252—1254). —This name is given by the author to monoxyphenanthrene, $C_{14}H_{10}O$, obtained by treating phenanthrene with the calculated quantity of fuming sulphuric acid, converting the resulting monosulphonic acid into ammonium salt, and fusing the latter with potash. The product crystallises from a mixture of benzene and petroleum-spirit in fine laminæ, which exhibit a bluish fluorescence, and melt at 112°.

Phenanthrol dissolves easily in alcohol and ether, less easily in benzene, and slightly in water. On exposure to air it acquires a red to brown colour. Alkalis dissolve it easily, forming crystalline compounds, which are readily soluble in water.

With acetic and benzoic anhydrides phenanthrol forms ethers which crystallise well. The acetyl-compound, $C_{14}H_9O(C_2H_3O)$, obtained by heating phenanthrol to 150° with acetic anhydride, crystallises from alcohol in brilliant laminæ which melt at 117—118°. Other compounds are being examined. J. R.

Phenenthrene-carbonic Acid. By F. R. JAPP and G. SCHULTZ (*Deut. Chem. Ges. Ber.*, 1661—1663).—This substance is obtained by distilling the potassium salt of phenanthrene-sulphonic acid with potassium ferrocyanide, saponifying the resulting nitril with alcoholic potash, and acidifying the solution with hydrochloric acid, which throws down the phenathrene-carbonic.acid in bulky white flocks. It is nearly insoluble in water, but dissolves easily in alcohol, ether, and glacial acetic acid, melts at 260°, and sublimes with partial decomposition. Its alkali-salts are easily soluble in water. The barium salt, $(C_{14}H_9COO)_2Ba + H_2O$, dissolves easily in hot water, and crystallises therefrom in tufts of needles.

The acid yields phenanthrene by distillation with soda-lime. It is converted, by oxidation with chromic and acetic acids, into *phenanthrene-quinone-carbonic acid*,



$$\begin{array}{l} OC—C_6H_3.COOH \\ \;|\quad\;\;| \\ OC—C_6H_4 \end{array}$$

J. R.

Anthraflavone, and a new Dioxyanthraquinone. By E. SCHUNK and H. ROEMER (*Deut. Chem. Ges. Ber.*, x, 1225—1227).—Anthraflavone, as prepared by Barth and Senhofer (*Liebig's Annalen*, clxx, 100), and by Rosenstiehl (*Compt. rend.*, lxxix, 768 and lxxxii, 1392), contains two substances separable by means of bartya-water, or better, benzene. The substance insoluble in benzene is anthraflavic acid; that insoluble in benzene is a new dioxyanthraquinone, called by the authors *metabenzdioxyanthraquinone*.

The new body differs from anthraflavic and iso-anthraflavic acids in the following respects:—(1) It melts at 291—293°; (2) it dissolves in potash with fine yellow colour; (3) it dissolves easily in glacial acetic acid; (4) it crystallises from weak spirit in anhydrous needles, (5) its calcium salt is nearly insoluble.

Besides the foregoing, anthraflavone contains a small quantity of a third substance, which dissolves with fine purple colour in strong sulphuric acid. J. R.

Pseudopurpurin. By C. LIEBERMANN and H. PLATH (*Deut. Chem. Ges. Ber.*, x, 1618—1620).—The authors' experiments on this substance confirm Rosenstiehl's conclusion, that it is a purpurin-carbonic acid, $C_{14}H_4(OH)_3.O_2.CO_2H$. They found that the difficulty hitherto experienced in obtaining the substance in the pure state may be overcome by exhausting crude pseudopurpurin repeatedly with chloroform, and then crystallising the residue from the same liquid.

Pure pseudopurpurin forms small red laminæ, which melt at 218—220°. When heated in a current of air it breaks up into purpurin and carbon dioxide, as previously stated by Rosenstiehl and by Plath. The decomposition is quantitive.

Pseudopurpurin, when heated for a short time with potash-ley, is completely converted into purpurin. The reaction affords a ready means of obtaining large quantities of purpurin from the crude substance, which contains much pseudopurpurin.

When bromine is added to pseudopurpurin or crude purpurin suspended in boiling water, carbon dioxide is evolved, and *monobromopurpurin*, which crystallises in fine red needles melting at 275°, is produced. The reaction with pseudopurpurin is as follows:—

$$C_{15}H_8O_7 + Br_2 = C_{14}H_7BrO_5 + CO_2 + HBr.$$

J. R.

New Colouring Matters derived from Anthracene. By M. PRUD'HOMME (*Bull. Soc. Chim.* [2], xxviii, 62—64).—A mixture of alizarin, glycerin, and sulphuric acid is heated for some time to 200°, when a rapid evolution of gas takes place, and the mixture assumes a dark brown colour. The mass is treated with water, and the insoluble residue exhausted with cold dilute alcohol, in which the colouring matter is dissolved. It gives coloured solutions similar to those of alizarin, which it resembles in its physical properties. Its alkaline solutions, however, are coloured orange, whilst those of alizarin are purple. On addition of alcohol to an alkaline solution it becomes dichromatic, being red in transmitted and green in reflected light.

If mononitroalizarin be treated in a similar manner, a residue is obtained containing two colouring matters; one, which is soluble in dilute alcohol, gives with alumina and strong iron mordants, precipitates resembling those of alizarin; but with weak iron mordants a bluish-grey precipitate resembling indigo.

The insoluble portion gives with alumina a brown precipitate, and resembles alizarin in most of its properties. These two colouring matters are not attacked by soap, feebly by chlorine, but are completely destroyed by acids.

The author is inclined to consider these bodies as glycerides, but he has come to no definite conclusions as to their constitution.

L. T. O'S.

A New Dye-stuff. By A. W. HOFMANN (*Deut. Chem. Ges Ber.*, x, 1378—1381).—There has lately been introduced into the trade a new bright red dye-stuff, which occurs as a somewhat crystalline powder, and consists of the sodium salt of an organic acid, generally mixed with a quantity of clay. It dissolves pretty readily in hot water, and less easily in hot alcohol, to a deep brown solution; it is insoluble in ether, and bears a somewhat high temperature without decomposition, but swells up at a stronger heat, yielding a large quantity of charcoal.

The author prepared from the sodium salt the pure acid, the analysis of which led to the formula $C_{16}H_{12}N_2SO_4$. It crystallises in brown-red needles, which are moderately soluble in water, easily soluble in alcohol, but insoluble in ether. Alkalis dissolve it to a brown colour; the aqueous solution gives a bright red crystalline precipitate with silver salts, and a crystalline precipitate with barium and calcium salts, the analyses of which prove it to be a monobasic acid.

The author discusses the constitution of the substance, and believes it to be nearly allied to chrysoïdin. By acting with one molecule of sulphonaphthol on one molecule of diazobenzene, thus: $C_{10}H_8SO_4 + C_6H_4N_2 = C_{16}H_{12}N_2SO_4$, he obtained a body which had the same composition and similar properties to the dye-stuff. The two, therefore, appear to be identical. T. C.

The Terpenes of Swedish Wood-tar from *Pinus sylvestris*. By Albert Atterberg (*Deut. Chem. Ges. Ber.*, x, 1202—1208).—Crude wood-oil ("holzoel"), the most volatile portion of the tar formed in the dry distillation of pine-wood in Sweden, when treated with potash to free it from creasote and acids, and afterwards submitted to fractional distillation, yields, amongst other products, the two following:—

1. A terpene boiling at 156·5—157·5°, and having the physical and chemical properties of australene.
2. A terpene boiling at 173—175°, and differing from all known terpenes. This the author calls *sylvestrene.*

These two bodies together form about 80 per cent. of the oil.

Sylvestrene is a clear liquid of sp. gr. 0·8612 at 16°, and has a peculiar odour resembling that of fresh pine. It turns the plane of polarisation to the right (rotation-coefficient for sodium light = 19·5°). With hydrochloric acid gas it forms a mono- and a dichlorhydrate, the former obtained by passing the gas into sylvestrene, the latter by passing the gas into an ethereal solution. The dichlorhydrate crystallises in brilliant needles, which melt at 72—73°, and dissolve easily in alcohol. It is decomposed by potash in a manner not yet clearly made out. J. R.

Euxanthone. By M. Salzmann and H. Wichelhaus (*Deut. Chem. Ges. Ber.*, x, 1397—1403).—By the action of sodium amalgam on euxanthone a white flocculent substance was obtained, which rapidly turned dark violet on exposure to the air. This body dissolves in alcohol and chloroform, forming a red solution; it is insoluble in ether, water, benzene, and petroleum ether. A very small quantity of the substance gives with excess of sulphuric acid a characteristic fuchsine-red coloration. It forms a red amorphous powder with acetyl chloride.

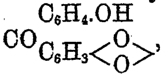
This reduction-product resembles a hydroquinone in its properties. No satisfactory formula could be found for it, but analysis shows that it contains more hydrogen than euxanthone.

The reduction of euxanthone by zinc-dust yielded a mixture of benzene, phenol, a small quantity of diphenyl, and a new substance having the formula $C_{13}H_8O$. This body crystallises in white scales, melting at 99°, boiling at 310—312°, soluble in alcohol, ether, chloroform, benzene, petroleum-ether, and carbon disulphide, and only slightly soluble in water. It is oxidised by ordinary nitric acid or potassium permanganate to $C_{13}H_8O_2$. This is a white substance, forming needle-shaped crystals, soluble in alcohol, ether, chloroform, benzene, and hot nitric acid, very slightly soluble in hot water and in petroleum-ether. It melts at 170—171°, and is not attacked by sodium amalgam or sulphurous acid.

A nitro-derivative, $C_{13}H_6O_2(NO_2)_2$ is formed by the action of fuming nitric acid on $C_8H_{13}O$ or $C_8H_{13}O_2$. It forms nearly colourless transparent leaves, soluble in benzene, melting at 260°.

The action of bromine on $C_{13}H_8O$ gives rise to two substitution-products, which can be separated by treatment with chloroform. $C_{13}HBr_7O$ is easily soluble in chloroform, benzene, ether, carbon disulphide, and petroleum-ether, less soluble in alcohol, and insoluble in water. It crystallises in pale-yellow oblique prisms, which darken at 130° and melt at 136°.

$C_{13}H_2Br_6O$ is less soluble than the preceding compound in the ordinary solvents. It forms lemon-coloured rhombic plates, which blacken at 220—230°, and do not melt at 280°.

Diacetyleuxanthone, $C_{13}H_6O_4(C_2H_3O_2)_2$, is prepared by heating euxanthone with excess of acetyl chloride to 100°, or with acetic anhydride to 150°, in sealed tubes. It crystallises in pale-yellow prisms, melting at 185°, soluble in benzene, alcohol, and chloroform, less soluble in ether, and insoluble in water. The existence of diacetyleuxanthone shows Baeyer's formula for euxanthone,  $CO\begin{matrix}C_6H_4.OH\\C_6H_3<\begin{matrix}O\\O\end{matrix}>\end{matrix}$, to be incorrect, the probable constitution being $CO(C_6H_3)_2O.(OH)_2$, *i.e.*, a carbonein of hydroquinone.

The product obtained by the action of zinc-dust is carbodiphenylene, $CO(C_6H_4)_2$, which was converted by oxidising agents into carbodiphenylene oxide, $CO(C_6H_4)_2O$. Attempts to prepare euxanthone synthetically were unsuccessful. W. C. W.

Quercetagetin. By LATOUR and MAGNIER DE LA SOURCE (*Bull. Soc. Chim.* [2], xxviii, 337—342).—The authors have isolated the yellow colouring matter of the flowers of the *Tagetes patula*. Its reactions in alcoholic solution are identical with those of quercetin; but it differs from this body in crystalline form and solubility in alcohol. The crystalline substance loses 4 mol. H_2O at 100°, and has then the composition $C_{27}H_{22}O_{13}$. The authors call in question the formula assigned by Hlasiwetz to quercetin, viz., $C_{27}H_{18}O_{12}$, for which they substitute $C_{27}H_{20}O_{12}$. Quercetagetin is thus quercetin + H_2O. This difference in composition confirms Hlasiwetz's view of the non-identity of the various quercetins. C. F. C.

Quassin. By G. GOLDSCHMIDT and H. WEIDEL (*Wien. Akad. Ber.*, lxxiv, 389—390).—The bark and wood of *Quassia amara*, L., yield when extracted with water a yellow resinous body, from which the crystalline compound described by Winkle, and more recently by Wiggers, could not be obtained. The resin darkens in colour on exposure to the air. It is split up into acetic and protocatechuic acids by fusion with caustic potash. W. C. W.

Cubebin. By H. WEIDEL (*Wien. Akad. Ber.*, lxxiv, 377—386).—Cubebin, $C_{10}H_{10}O_3$, forms silky white needle-shaped crystals, soluble in alcohol, benzene, and chloroform, m. p. 125°. Nitric acid converts this body into oxalic and picric acids. By the action of nitrous acid on cubebin, minute yellow crystals of $C_{10}H_9(NO_2)O_3$ are obtained, which dissolve in ether, alcohol, ammonia, and caustic potash. The potash solution has a purple-violet colour.

$C_{10}H_7Br_3O_2$ separates out when bromine is added drop by drop to a solution of cubebin in chloroform. It is insoluble in the ordinary solvents, but dissolves in boiling xylene, and is deposited on cooling in small white crystals. The bromine in this body cannot be replaced by hydroxyl. Fusion with caustic potash converts cubebin into carbonic, acetic, and protocatechuic acids. Although ferulic acid and eugenol yield the same products when decomposed by caustic potash, all attempts to convert cubebin into these bodies have failed.

W. C. W.

On Crystallised Ergotinine. By C. TANRET (*J. Pharm. Chim.*, xxvi, 320—324).—This alkaloïd occurs in the proportion of about 1 gram per kilogram of ergot of rye. When pure it forms white needles, insoluble in water, soluble in ether, chloroform, and alcohol. Either in the solid state or in alcoholic solution it absorbs oxygen rapidly from the air, and turns brown. The alcoholic solution is fluorescent, and when exposed to the air turns green and then brown; acid solutions turn red.

Ergotinine is a weak base, forming salts which are decomposed by addition of water or by evaporation; chloroform removes a part of the base. The sulphate is crystallisable.

When sulphuric acid, diluted with one-seventh of water, is added to a solution of ergotinine containing a little ether, a reddish-violet colour, changing to blue, is produced.

The author describes also another body contained in ergot. It is colourless, crystallisable, of camphor-like odour, and is volatile at the ordinary temperature: it is neutral, melts at 165°, boils at 209° (uncorrected), and sublimes in star-like groups of crystals. It is insoluble in water, soluble in alcohol and in chloroform. C. W. W.

The Albuminoïds of Seeds. By H. RITTHAUSEN (*Pflüger's Archiv. f. Physiologie*, xv, 269—288).—In his new work on Physiological Chemistry, Part I, p. 75, Hoppe-Seyler expresses views contrary to those held by the author with regard to the albuminoïds in seeds, and says that "the statements of Ritthausen relate not to purely unaltered albuminoïds, but to more or less destroyed or insufficiently purified bodies."

The author combats these statements, and maintains that Liebig's method of separating the albuminoïds of plant-seeds yields pure and unaltered materials, and that these albuminoïds are not similar to those found in the eggs of animals. F. J. L.

Cryptophanic and Paraphanic Acids. By J. L. W. THUDICHUM (*Pflüger's Archiv. f. Physiologie*, xv, 455—468).—In the course of his earlier investigations on the separation of these acids from human urine (*Chem. Soc. J.*, 1870, p. 116), the author observed that they were precipitated by ferric chloride. He has now made use of this property as a means of separating them, so as further to study their reactions. The urine having been made alkaline by addition of lime or baryta, is evaporated to $\frac{1}{4}$ its volume, and a solution of ferric chloride is added. This precipitates the cryptophanic and paraphanic acids as iron salts, together with some hippuric and benzoic acids. The iron salt can be decomposed by ammonia, baryta, or lime. Baryta does not completely destroy it, but nevertheless yields the purest product. Ammonium sulphide decomposes it completely, but the resulting cryptophanic acid contains sulphur. F. J. L.

Physiological Chemistry.

On the Mode of Formation of Sugar in the Liver. By C. BERNHARD (*Ann. Chim. Phys.* [5], xii, 397—405).—In a previous memoir (*Compt. rend.*, xli, Sept. 24, 1855, and *ibid.*, xliv, 578) the author has shown that the sugar in the liver owes its origin to the action of a diastatic ferment on glycogen; the present paper describes the preparation of glycogen and of this ferment from the liver.

The liver of a well-fed animal is cut in pieces and thrown into boiling water. The pieces are then pounded and again cooked for a few minutes. The liquid obtained by pressing the liver is treated with a small quantity of animal charcoal, which removes albuminoïd and biliary matter, leaving a mixture of glycogen and sugar. Alcohol precipitates crude glycogen from this solution; it may be freed from nitrogenous impurities by boiling with caustic potash, precipitating with alcohol, dissolving the precipitate in acetic acid, and reprecipitating with alcohol. This method of purification is adopted in preference to that of precipitation with the double iodide of potassium and mercury, as directed by Brücke (*Wien. Akad. Ber.*, lxiii, Feb. 1871).

Diastase is prepared thus: the liver of a dog which has fasted for some days, is washed by passing water through the *vena porta* until all the sugar and glycogen are removed. It is then minced and macerated for four days with five times its weight of glycerin. The mixture is filtered, and the diastase can be precipitated by alcohol; but it retains its power better when kept in solution in the glycerin. The diastase from barley and that from the liver are identical; and glycogen is identical with starch. Hence the mode of formation of sugar in animals and vegetables is identical.

The most general mode of formation is undoubtedly: 1st, the synthetical formation of amylaceous matter; 2nd, the transformation of the amylaceous matter into sugar. W. C. W.

On the Decomposition of Taurine in the Digestive Process. By C. O. CECH (*Deut. Chem. Ges. Ber.*, x, 1461—1464).—The author has investigated the modification in the composition of the excreta of fowls, brought about by the administration of taurine in solution. A considerable portion was found to reappear unchanged—no uramido-acids or hyposulphites could be detected. At the same time a considerable increase in the quantity of sulphuric acid evacuated was observed, and is referred by the author to the decomposition of the taurine. Failing to detect urea in the excreta, and observing an increased quantity of uric acid, he concludes that the equivalents of carbon and nitrogen resulting from the decomposition have passed over into uric acid. C. F. C.

On Certain Modifications of the Substance of Eggs Determined by Fungoid Growths from Without. By A. Bechamp and G. Eustache (*Compt. rend.*, lxxxv, 854—857).—From a series of observations on hen's eggs the authors draw the following conclusions:—

1. Infusoria are incapable of traversing the substance of the shell, which however is easily penetrated by microscopic hyphæ. These also traverse the lining membrane of the shell and develop freely on its internal surface.

2. While the membrane of the yolk is impenetrable by all microscopic organisms whatsover, changes are induced in its substance by the entrance of hyphæ into the surrounding mass, which are independent of organised ferments other than microzyms, and different from the ordinary true putrefaction of incubated eggs.

3. White of egg, under these conditions, develops an acid reaction, which is solely due to the mycelium of the fungus.

4. Development of bacteria in the yolk has been observed to occur concomitantly, and is referred to a process of evolution from the normal microzymes of the yolk, determined by the changes taking place in the medium. C. F. C.

Composition of the Cephalo-rachidian Liquid. By Yvon (*J. Pharm. Chim.*, xxvi, 240—242).—The liquid was neutral, lemon-yellow and slightly opalescent, owing to the presence of fatty matters. When shaken with ether, it lost its colour, and became transparent. Its density was 1·01.

It coagulated easily when heated, contained neither fibrin nor mucin, but small quantities of hydropisin (0·18 grm. per litre), albumin and metalbumin. Urea was also present, and traces of iron. The following is the analysis:—

Organic matter.	
Fat	0·366
Urea	0·275
Albumin (total)	3·560
Loss	0·059
	4·260

Ash.	
Phosphoric acid	0·563
Chlorine	4·301
Lime	0·122
Magnesia	0·238
Alkalis and loss	3·688
	8·912

C. W. W.

Chemistry of Vegetable Physiology and Agriculture.

Formation of Starch in the Cells of Plants excluded from Light. By JOSEF BÖHM (*Deut. Chem. Ges. Ber.*, x, 1804—1807).—By experiment upon plants of *Phascolus multiflorus*, the author shows the common statement, that the starch of chlorophyll-grains is in all cases the product of an intrinsic synthesis from carbonic anhydride and water, to be fallacious. From the experiments in question follow two important positive conclusions: 1. That the formation of starch in chlorophyll-grains, is in many cases the result of a metamorphosis of bodies, not intrinsic to the cells in which this conversion takes place, but elaborated elsewhere by the plant; and 2. That this process of conversion is entirely independent of the action of light.

C. F. C.

Nitrogenous Constituents of Mangold-wurzel. By E. SCHUZE and A. URICH (*Landw. Versuchs-stat.*, xx, 193—245).—I. *The Amides of Mangold-juice.*—In a former communication (this *Journal*, 1876, i, 419) it was shown that beet-roots are richer in amides than in albuminoïds. Of the total nitrogen present in two varieties, 21·6—38·9 per cent. existed as albuminoïds, and 34—47·7 per cent. as amides.

Besides albumin, the only organic nitrogenous compound obtained from the juice was betaine, and a substance which, like asparagine, decomposed with formation of ammonia when the juice was boiled with hydrochloric acid; asparagine, which is present in sugar-beet, was not detected in the mangolds. With a view of separating out the second nitrogenous substance above mentioned, the juice from beetroot was precipitated with a slight excess of lead acetate, and the precipitate so obtained was decomposed with hydrochloric acid. After precipitating the excess of hydrochloric acid with a concentrated solution of lead acetate, and filtering off the chloride thus formed, the filtrate was saturated with lead acetate. When a bulky precipitate formed soluble in excess, this solution was mixed with a large quantity of alcohol, whereupon the lead compounds separated out and were removed. On decomposing the lead salts with hydrosulphuric acid, and removing the last traces of hydrochloric acid with oxide of silver, the solution on concentration gave crystals of amido-acids. Finally these were separated into two different substances, A and B, the former, which separated out first, consisting of scaly crystals and sometimes regular tetrahedrons, while B, which separated from the last mother-liquors, crystallised in very thin soft laminæ. These two substances were purified by conversion into copper salts, when, on decomposition with hydrosulphuric acid, the amido-acids were obtained in the pure state. A gave on analysis the formula, $C_5H_9NO_4$, corresponding with glutanic acid: the crystals melted at 188—190°, which led to the supposition that they consisted of some isomeric body, for glutamic acid melts at 135—140°. On further investigation, however, the crystals were found to be identical with glutamic acid.

B was found to consist of aspartic acid.

Mangold-juice therefore contains, besides albumin and nitrates, the ammonium salts of glutamic acid and aspartic acid, together with betaine. It is probable that there is no other nitrogenous body present, except in traces. The juice from mangolds of 1875 gave on an average ·0525 per cent. of amido-acids = 4·5—4·6 grms. of glutamic acid per litre. By Sachsse and Kormann's method it was always found that the nitrogen came out too high.

The fresh matter of the root reduced to pulp gave :—

	Roots of 1874.	Roots of 1875.
Soluble albuminoïds .	0·2306 p. c. = 0·0369 p. c. N.	0·1413 p. c. = 0·0226 p. c. N.
Insoluble.	0·0950 p. c. = 0·0152 „	0·1023 p. c. = 0·0164 „
Glutamine (and asparagine)	0·4066 p. c. = 0·0780 „	0·4425 p. c. = 0·0847 „
Betaine	0·1359 p. c. = 0·0161 „	0·0226 p. c. = 0·0027 „
Nitric acid	0·3363 p. c. = 0·0872 „	0·2483 p. c. = 0·0644 „
Ammonia	0·0080 p. c. = 0·0066 „	0·0085 p. c. = 0·0071 „
	Total. . . . . . 0·2400 p. c. N.	Total. . . . . . 0·1979 p. c. N.

[*Note by Abstractor.*—In 1874 experiments were made in the laboratory of the Agricultural College, Cirencester, upon the direct determination of nitrogen existing in the form of albumin, contained in various roots. The albumin was precipitated in a warm solution with carbolic and tannic acids, in presence of alcohol; a combustion was then made with the precipitate so obtained.]

II. *Changes of the Nitrogenous Constituents in the Second Year of Growth.*—Pfeffer has proved that in seedlings the asparagine formed from albumin during germination, is afterwards reconverted into this substance (*Landw. Versuchs-stat.* v, 101). Experiments were made with beet-root to see whether the amides contained in it change in a similar manner, and also to determine the behaviour of the other nitrogenous constituents.

Experiments of 1875.—Some beets of 1874 were planted in river sand freed from nitrogenous matter by washing and then heating to redness. The roots were kept under cover and watered with distilled water; vegetation soon commenced, and although not vigorous, the stems reached a length of 50—55 centimeters, and blossoms formed, the leaves however being small. The total weight of vegetable matter produced, as was to be expected, was not great. For every 1,000 grams of root only 10·04 grams of dry substance (leaves, stems, &c.) was obtained; this was very rich in nitrogen, containing on an average 6·59 per cent. The amount of nitrogen present in the roots before forcing was about ·23 per cent., so that rather over one quarter of the total nitrogen had gone to the leaves, &c.

While the roots lost a quantity of amides during growth, still no gain in albumin was detected; but as the experiments were carried out on a small scale only, too much reliance must not be placed on the results. The action of the nitrates still remains undetermined. Of the total nitrogen present, 91 per cent. was in the form of amides.

Experiments of 1876.—Roots from the crop of 1875 were planted in good soil, and after growth the juice was expressed from them, and analysed with the following results:—

	Nitrogen.					
	Existing as ammonia.	Existing as amides.	Existing as glutamine (and asparagine).	Glutamine (and asparagine).	Betaine.	Coagulable albumin.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Root 1	—	0·1166	—	—	—	—
" 2	—	0·1049	—	—	—	—
" 3	—	0·0094	—	—	—	—
" 4	—	0·1179	—	—	—	—
" 5	—	0·0871	—	—	—	0·1163
" 6	—	0·1337	—	—	—	0·1794
" 7	—	0·0828	—	—	—	0·1375
" 8	0·0092	0·0991	0·0802	0·4182	—	—
" 9	0·0077	0·1222	0·1110	0·5781	—	—
" 10	0·0049	0·0993	0·0874	0·4557	—	—
" 11	0·0071	—	0·0794	0·4140	—	—
" 12	0·0082	—	0·0796	0·4151	—	—
" 13	0·0066	—	0·0784	0·4088	—	—
" 14—16	0·0065	—	0·0858	0·4474	—	—
" 17—19	0·0076	—	0·0888	0·4630	—	—
" 20—22	—	—	—	—	0·0250	—
" 23—25	—	—	—	—	0·0212	—
Mean....	0·0072*	0·1063	0·0864	0·4518	0·0231	0·1444

In roots 14—16, 17—19, 20—22, and 23—25, the samples were mixed.

The fresh roots contained, in a mean of six determinations, ·2483 per cent. of nitric acid (N_2O_5): a mean of three determinations gave ·1023 per cent. of insoluble albumin—the percentage of the nitrogen existing as insoluble albumin was multiplied by the constant 6·25 to give this figure—and in the pulp 2·05—·797 per cent. of nitrogen was found.

With roots grown from the seed, the fresh juice contained, as a mean of five analyses:—

Nitrogen.			
Existing as ammonia.	Existing as amides.	Existing as glutamine (and asparagine).	Glutamine (and asparagine).
Per cent.	Per cent.	Per cent.	Per cent.
0·0034	0·0356	0·0266	0·1388

* 0·0087 NH_3.

Betaine was found to diminish in quantity as the roots grew; for in an experiment made with roots containing ·008 per cent. of betaine, hardly a trace could be detected after they had been planted and allowed to mature. The following table shows that but little nitric acid passes from the root to the leaves, &c., during growth, although a decided loss of this substance is observed.

Weight of the Roots, in grams.		Weight of the vegetable matter produced, dry.	N_2O_5 contained in the Root.		N_2O_5 in dry vegetable matter.
Before planting.	After growth of leaves, &c.		Before planting.	After growth.	
			Per cent.	Per cent.	
1296	1267	11·46	0·2171	0·1931	0·05
1211	1164	13·83	0·2231	0·1824	trace
963	918	8·86	0·2377	0·1559	0·17

Corenwinder is making investigations similar to those above given, with which probably his results will be found to agree (Stammer, *Jahresber. f. Zuckerfabrikation*, Bd. vli, s. 88).

The paper concludes with an analytical supplement, giving the author's results in a tabular form; the number of analyses performed is very large. R. C. W.

Cultivation of the Rough-haired Soja-bean (*Soja hispida*, Mönch). By F. HABERLANDT (*Landw. Versuchs-stat.*, xx, 247—272). —Although the soja-bean contains more nutritious material than other seeds of a like nature, its cultivation has been hitherto neglected in Europe. It is grown in the Malay Islands (Java), India, China, and Japan; and in the two latter is used as an every-day food.

Seeds obtained from various sources were planted, and the plants were grown in three plots, each plant having a space of 4·03 square decimeters. Time of collecting seed June and September:—

	Number of Plants.	Grams of Seed obtained.	Weight in Grams of 1000 of the original Beans.	Weight in Grams of 1000 of the reproduced Beans.	Sp. gr. of the original Beans.	Sp. gr. of the reproduced Beans.
Plot No. I, brown-red variety, from China	27	249·2	105·0	154·5	1·204	1·233
Plot No. II, light yellow variety, from China	25	336·5	92·5	148·0	1·190	1·246
Plot No. III, light yellow variety, from Mongolia	15	196·9	81·5	126·0	1·172	1·241

On comparing these beans with the original from China and Mongolia they were found to be heavier and larger. The percentage increase in weight was for No. I, 54·7; No. II, 47·1; No. III, 60.

The following table gives results obtained from plants produced from the original seeds, as well as from those produced by replanting the beans thus yielded:—

	Yellow Soja-bean from Mongolia. (Reproduced.)	Yellow Soja-bean from China. (Reproduced.)	Brown-red Soja-bean from China. (Reproduced.)	Black Soja-bean from China. (Original.)	Black Soja-bean from China. (Reproduced.)	Black Soja-bean from Mongolia. (Original.)	Black Soja-bean from Japan. (Original.)
Size of plots in square meters	9·60	9·60	9·90	4·0	11·0	4·0	4·5
Time of sowing	25 Ap.	25 Apr.	25 Apr.	5 May	25 Apr.	5 May	5 May
Sprouts shown	19 May	19 May	19 May	2 June	19 May	2 June	2 June
Commencement of blossoming	26 June	23 June	20 June	28 June	26 June	3 July	3 July
Harvest......	26 Sept.	1 Oct.	1 Oct.	6 Nov.	6 Nov.	6 Nov.	6 Nov.
Number of plants yielded	268	278	339	52	245	70	72
Weight of seed in grams	2707	3710	1950	650	2180	570	500
Weight of air-dried straw in grams	4300	7270	4150	1920	5030	2410	2200
Number of seeds from 1 plant	61·7	93·3	40·5	124·4	80·4	79·8	65·7
Weight of 1000 air-dried seeds	163·6	143·0	141·8	101·6	110·6	102·0	105·7

General Analyses of Seeds.

	In 100 parts of the Air-dried Substance.			Calculated on substance with 10 per cent. of Water.		
	In the original Seed.	In the Seed after 1st reproduction.	In the Seed after 2nd reproduction.	In the original Seed.	In the Seed after 1st reproduction.	In the Seed after 2nd reproduction.
Yellow variety from Mongolia.						
Water	7·14	9·36	7·89	10·00	10·00	10·00
Protein	32·15	32·07	32·58	31·41	31·85	31·90
Fat	17·10	17·59	17·49	16·69	17·47	17·11
Non-nitrogenous extractive matter	32·91	31·59	—	33·14	31·35	—
Fibre	4·58	4·48	—	4·47	4·45	—
Ash	5·42	4·91	—	5·29	4·88	—
Yellow variety from China.						
Water	7·96	8·62	7·89	10·00	10·00	10·00
Protein	31·26	34·81	34·97	30·56	34·37	34·33
Fat	16·21	18·53	18·39	15·81	18·25	18·00
Non-nitrogenous extractive matter	34·59	28·84	—	33·80	28·32	—
Fibre	4·75	4·37	—	4·67	4·30	—
Ash	5·23	4·83	—	5·12	4·76	—
Brown-red variety from China.						
Water	7·46	9·78	8·68	10·00	10·00	10·0
Protein	33·26	33·17	32·47	32·35	33·09	22·03
Fat	17·45	18·42	18·05	16·87	18·38	17·81
Non-nitrogenous extractive matter	31·78	29·62	—	31·00	29·54	—
Fibre	5·31	4·02	—	5·17	4·01	—
Ash	4·46	4·99	—	4·34	4·98	—

These analyses correspond very closely with those made by Zenff in 1872.

The soja is the richest in fat and oil of all beans.

An analysis of the ash of the yellow variety from China, second reproduction, gave (free from C and CO_2) per cent. of—

K_2O	Na_2O.	CaO.	MgO.	Fe_2O_3 and Al_2O_3.	P_2O_5.	SO_3.	Cl.	SiO_2.
44·56	0·98	5·32	8·92	trace	36·89	2·70	0·27	trace

The air-dried seed contained 2·87 per cent. of ash, and dried 100° 3·14 per cent. The proportion of K_2O agrees with that in horse-beans, garden-beans, and peas. An analysis of the air-dried straw gave: moisture, 12·44 per cent.; protein, 9·43; ether extract, 2·51; extractive matter free from nitrogen, 36·03; fibre, 29·45; ash, 10·14. 100 parts of the pure ash gave:—

K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3 and Al_2O_3.	P_2O_5.	SO_3.	Cl.	SiO_2.
15·41	2·18	14·47	15·42	0·75	9·32	6·37	0·16	5·41

The protein in this straw is about the same as in pea-straw, and twice as much as in the straw from lupine.

The oil much more than in pea, bean, or lupine straw.

The K_2O in ash much less than in pea, bean, or lupine straw.

The CaO and MgO in ash much more than in pea, bean, or lupine straw.

The P_2O_5 in ash the same as in pea, bean, or lupine straw.

The paper concludes with a series of tables on the temperature of the soils in which the bean was cultivated. R. C. W.

Functions of Vine Leaves. By H. MACAGNO (*Compt. rend.*, lxxxv, 763—765)—The leaves of the vine act as organs of secretion, more especially those at the upper extremities of the fruit-bearing branches, secreting glucose and cream of tartar, which are conducted along the branches to the fruit, to which they act as nutrients. This accounts for the occasional failure of the vine crops after the operation called "pincement," which consist in removing the ends of the fruit-bearing branches at the third or fourth leaf above the highest bunch of grapes. This operation, if carried on to too great an extent, especially where the production of grapes is abundant, does not leave a sufficient amount of leaves for the secretion of the quantity of nutriment required by the fruit. L. T. O'S.

Influence of Gases on Fermentation. By OTTO NASSE (*Pflüger's Archiv. f. Physiologie*, xv, 471—481).—Experiments were made on invertin as follows:—An ice-cold mixture of cane-sugar solution and invertin was divided into five parts, and through each of four of them a special kind of gas passed; through the fifth common air. The mixtures were in all cases subject to exactly similar conditions, and the results were:—inverted sugar amounted with oxygen and carbonic oxide, to 0; with hydrogen to 8 mgm., with CO_2 to 20 mgm., and with air to 7 mgm. This last result was proved by a subsequent experiment to be partly due to the carbonic acid in the atmosphere.

Experiments upon ptyalin and glycogen solution show that in this case the gases exert but slight influence over the power of the ferment.

The ferment was not in any case destroyed by the action of the gas.

Applying this method of research to muscular tissue, a larger amount of carbohydrates was found in muscle which had been kept in an atmosphere of carbonic acid, than in muscle left exposed to the air under otherwise similar conditions. F. J. L.

Analytical Chemistry.

Contributions to Volumetric Analysis. By G. FLEURY (*J. Pharm. Chim.*, xxvi, 329).—*Estimation of Sulphuric Acid.*—A modification of Boutron and Boudet's hydrotimetric method for the estimation of sulphuric acid in water. The author recommends a greater dilution of the barium nitrate solution, and the expulsion of all the carbonic acid by the addition of hydrochloric acid and boiling. The whole process is given in detail.

Estimation of Magnesia.—After precipitation of the lime in the usual way, the excess of ammonium oxalate is destroyed by boiling with sulphuric acid; ammonia, ammonium chloride, and a known quantity of sodium phosphate are added (in such quantity that there shall be at least 0·1 gram phosphoric acid in excess), and the liquid is made up to a known volume, and left for twelve hours.

From 20 to 30 c.c. of the clear solution (containing 0·1 gram H_3PO_4) are then titrated with uranium nitrate, with the precautions recommended by Joulie. C. W. W.

Use of Bromine in Gas Analysis. By M. BERTHELOT (*Ann. Chim. Phys.* [5], xii, 297—302). The gas is collected over water in a graduated tube of 15—20 cb.c. capacity provided with a cork through which a capillary tube passes. A small tube containing not more than half a cb.c. of bromine is brought into the graduated cylinder, and the cork with the capillary tube is inserted. The apparatus is now held in a slanting position and gently shaken, in order to bring the bromine vapour in contact with the gas. After the bromine vapour has filled the cylinder, the cork is removed, allowing the liquid bromine in the small tube to escape. The bromine vapour is absorbed by solid caustic potash, and the volume of residual gas measured. W. C. W.

Estimation of Gases dissolved in Water. By FELIX BELLAMY (*J. Pharm. Chim.*, xxvi, 324—329)—The author finds it advantageous, in cases where the determination of the gases cannot be immediately performed, to add to the water a small quantity of one of the following solutions:—(1) 8 or 10 c.c. of a saturated solution of alum and 3—5 c.c. of ammonia per litre of water; (2) 5 c.c. of a 6 per cent. solution of aluminium sulphate (as alum) with 3—5 c.c. of ammonia per litre of water; (3) 5 c.c. of an 8—10 per cent. solution of zinc sulphate with 3—5 c.c. of ammonia per litre of water. Ammonia alone produces the same effect, though not so thoroughly.

The action of these solutions probably depends upon the precipitated alumina or zinc hydrate rendering insoluble the organic matter present in the water. The action of ammonia alone is not so easily explained.

A series of tables is given, showing the action of these solutions in preventing the loss of oxygen on standing. The author draws the following conclusions from these tables:—

(1) If water containing organic matter be kept in corked flasks, the oxygen disappears gradually and completely, the carbonic acid at the same time increasing.

(2) In water to which alum and ammonia have been added the oxygen remains the same, even after eighteen days' standing, whilst in natural water, after eleven days, the oxygen had diminished by more than half. C. W. W.

On the Determination of Cuprous Oxide present in Copper. By C. RAMMELSBERG (*Deut. Chem. Ges. Ber.*, x, 1780—1781).—By digesting cuprous oxide with a solution of silver nitrate in excess, in addition to metallic silver, an insoluble basic copper nitrate is formed. The author has determined the empirical constitution of this salt to be $Cu_{10}N_6O_{25}$. The reaction by which it is formed appears to be the following:—

$$7Cu_2O + 14AgNO_3 = 7Ag_2 + 4Cu(NO_3)_2 + Cu_{10}N_6O_{25}.$$

At the same time it is probable that the composition of the basic nitrate may vary with the conditions of its formation. The reaction in question cannot, therefore, be employed for the estimation of cuprous oxide. C. F. C.

Note on the Estimation of Mineral Poisons. By N. SOKOLOFF (*Bull. Soc. Chim.* [2], xxviii, 348).—The author states that the organic constituents of a dead body are never completely decomposed by the methods of oxidation usually practised. To attain this end, and therefore to ensure the complete isolation of mineral poisons, the transparent liquid mass obtained by treating the intestines with hydrochloric acid and potassium chlorate is evaporated to dryness, and the residue heated to redness in a crucible, with addition of a small quantity of potassium nitrate in place of chlorate.

The author has employed this method for the estimation of zinc, copper, and lead, in cases of poisoning by compounds of these metals. C. F. C.

Presence of Ammonia in Tartrates. By E. HOLDERMANN (*Arch. Pharm.* [3], xi, 44—46).—The author had occasion to prepare a Fehling's solution, and observed the smell of ammonia on dissolving the tartrate in a hot solution of caustic soda. Analysis showed that the sample, although approved by the German pharmacopœia, and manufactured by a well known chemical firm, contained ammonia to the extent of 0·355 per cent., present as chloride. The author concludes from this that a chemical preparation may correspond with all that the pharmacopœia requires, but may at the same time contain substances which render its use for analytical purposes quite impossible.

In this case, for instance, the presence of ammonia greatly influenced the success of the reaction of Fehling's solution on sugar. D. B.

Testing of Red Wine. By K. Calmberg (*Arch. Pharm.* [3], xi, 47).—The author mentions that in *Buchner's Repert*, 1876, 11 and 12, a process is described which has been reprinted from the *Jahresbericht des Phys. Vereins*, Frankfort-on-the-Maine, 1874–75. It is stated that by diluting 10 c.c. of genuine red wine with 90 c.c. of distilled water, and adding 10 c.c. of a concentrated solution of sulphate of copper, a scarcely visible greenish coloration is obtained, whereas wine prepared with mallows shows within a few minutes a pure blue to bluish-violet colour. The author states that this is not correct, and that the same result is obtained in both cases. D. B.

Examination of Wine as to the Presence of Glycerin, Colouring Matter, &c. By E. Reichardt (*Arch. Pharm.* [3], xi, 142—152). In these investigations the following points were determined:—(1.) The *specific gravity*. This varied from 0·99 to 1·02, with the exception of champagne, which has a density of 1·042. (2.) The *percentage of acid.* This is referred to a monobasic acid calculated as tartaric acid. (3.) *Alcohol; residue on evaporation; ash.* 200 grams or 200 c.c. were distilled until two-thirds of the volume had come over. The alcohol was determined in the distillate in the usual manner, while the residue in the retort was evaporated at 100° and weighed until constant in weight. Thus the residue on evaporation was obtained, while after igniting the former the ash remained. (4.) *Glycerin.* The wine or a certain portion of the evaporated residue was evaporated with an excess of slaked lime, and the residue treated several times with 90 per cent. alcohol. In the case of pure wine, perfectly pure colourless glycerin remains; the same is the case with red wines. Gallised wines, however, yield partly gelatinous, partly turbid solid residues, which have to be separated once more by a mixture of alcohol and ether. Glycerin is deposited in this solvent, while the foreign constituents remain in the residue. (5.) *Colouring matter of red wine.* Gautier's method again proved to be the best and most certain test for investigating wines as to their colouring matter (*Arch. Pharm.*, 486).

The author then proceeds to give a full account of the various analyses of wines, the results of which may be tabulated as follows:—

Quality.	Sp. gr.	Acid.	Alcohol.	Extract.	Ash.	Glycerine.
Rhine Wines.						
Nierst. Kranzb., 1875	0·994	0·410	9·95	2·794	0·260	1·326
Nackenheimer, 1874	0·993	0·420	8·63	2·536	0·216	0·978
Nierst. Brudersb., 1874 (Aulese)	0·993	0·533	9·90	2·268	0·288	1·368
Michelsb. Aulese, 1874	9·990	0·495	11·00	2·500	3·188	1·158
Rauenthaler, 1874	0·096	0·683	8·63	3·020	0·210	1·196
Nierst. Rehbach, 1874	0·095	0·580	9·69	4·195	0·250	1·498
Hochheimer Berg., 1870	0·993	0·713	9·90	2·630	0·214	0·978
Gräfenberger, 1868	1·000	0·517	9·90	4·390	0·190	1·664

Quality.	Sp. gr.	Acid.	Alcohol.	Extract.	Ash.	Glycerine.
French Red Wines.						
St. Estèphe, 1874	0·997	0·600	9·00	2·976	0·280	1·038
Cautanec, 1874	0·995	0·600	7·88	2·608	0·236	1·408
Gr. Moulis, 1875	0·995	0·600	10·13	2·380	0·240	0·874
Ponjeaux, 1875	0·995	0·600	8·63	2·534	0·216	1·102
French White Wines.						
Barsac, 1869	1·020	0·430	10·50	5·020	0·410	1·537
Sauternes, 1865	0·996	0·592	10·88	3·700	0·295	1·150
Auction Wines.						
Red wine	0·992	0·980	9·65	2·376	0·190	0·620[*]
Champagne	1·042	0·600	12·00	15·246	0·165	0·090[†]
Jena Wines.						
White wine, 1871	0·994	0·507	7·88	2·250	0·230	0·543
Ditto, 1874 (with root sugar)	0·998	0·615	5·25	1·950	0·262	0·322[‡]
Ditto, 1874 (with starch sugar)	1·006	0·473	6·57	3·850	0·180	0·540
Red wine, 1875	0·999	0·600	4·20	2·230	0·275	0·435
Frankfurt Apfelwein.						
1875	1·000	0·483	4·40	2·413	0·394	0·744

The above comparison shows that the more northern wine regions of Germany produce a much smaller quantity of glycerin, and that the presence of the latter determines the origin of wines. Although it seems probable that now and then a certain relation exists between alcohol and glycerin, or between residue and glycerin, it is nevertheless impossible to obtain certain data for comparison. With regard to good, strong, unadulterated Rhine wines and Bordeaux wines, the quantity of glycerin should be from 1 to 1·5 per cent.

By treating the evaporated residues of unadulterated wines with lime and alcohol, pure glycerin is obtained. By treating wines gallised with starch-sugar in a similar manner a mixture of glycerin and a body resembling dextrin is obtained. This body is no doubt identical with that observed by Neubauer. It may be separated by a mixture of ether and alcohol. With regard to the optical properties of this body, some differences were always noticed. By examining wines directly as to the polarisation, they often showed different results, more especially the above wine, which polarised distinctly to the left. Although these optical investigations have yet to be followed up further, they are likely to promise useful results.

D. B.

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[*] Also 0·650 per cent. solid, similar to dextrin.

[†] Also 0·190 per cent. solid, similar to dextrin.

[‡] Also 0·100 per cent. solid, similar to dextrin.

The Estimation of Casein and Fat in Milk. By J. LEHMANN (*Liebig's Annalen*, clxxxix, 358—367).—Five grams of milk diluted with an equal weight of distilled water are allowed to flow slowly from a pipette on to a porous earthenware plate standing over sulphuric acid, but covered with a clock-glass to prevent the evaporation of the milk. The pores of the plate must be so small as not to admit the passage of the smallest milk-globule, the diameter of which is 0·001 to 0·025 millimeter. In two hours the serum of the milk will be absorbed by the plate, leaving behind the casein and fat. This residue is removed by the aid of a sharp horn spatula, dried for two hours at 105°, and weighed. The fat is dissolved out in the usual way with ether, the residue, consisting of casein and mineral matter, is weighed, then ignited, and the weight of ash deducted from the weight of casein and ash.

This method gives good results; the fat determinations agree with those made by the ordinary process of evaporating to dryness and extracting with ether; but the amount of casein is higher than that which Hoppe-Seyler obtains by precipitating with acetic acid. The great drawback to the process is the difficulty of obtaining plates possessing the requisite degree of porosity. W. C. W.

Technical Chemistry.

Separation of Carbon, Silicon, Sulphur, and Phosphorus in the Refining and Puddling Furnace, and in the Bessemer Converter. By I. L. BELL (*Journal of the Iron and Steel Institute*, 1877, 390; *Dingl. polyt. J.*, ccxxv, 264—268, 351—357).—Exposed to the intensely deoxidising agency of the blast-furnace, portions of the silica, and probably the greater part of the sulphur compounds, lose their oxygen and are taken up by the reduced iron. Practically the whole of the phosphorus is found in the metal.

In the primitive low furnace of the Catalan type, the deoxidising agency is insufficient to reduce the ore completely, and silicon, sulphur, and phosphorus are almost absent from the resulting iron. Experiments on the direct process conducted by Siemens show that the ore is imperfectly reduced, and that most of the phosphorus goes into the slag, for the slag was found to contain 36·51 per cent. of metallic iron, and 2·24 per cent. of phosphorus, whilst the resulting iron gave Fe 99·71, C 0·12, Si 0·065, S 0·027, P 0·074. Cleveland pig puddled in a Danks' furnace gave a close approximation in the percentage of phosphorus.

Experiments on the refining of pig iron made at the Bowling Works with Bowling cold-blast pig containing C 3·686, Si 1·255, S 0·033, P 0·565, showed that the loss per cent. was as follows:—C 9·33, Si 88·05, S 24·24, P 13·27. A second series of experiments gave an average loss per cent. of C 8·89, Si 90·12, S 29·77, P 48·12. A charge of Clarence No. 3 hot-blast pig, containing C 3·12, Si 2·80, S 0·11, P 1·47, showed on refining a loss per cent. for the C 19·87 Si 90·57, S 100, P 42·85.

The difference between refining and the Bessemer process is one of appearance only; in principle there is a close resemblance. In both cases the silicon is most speedily driven off, but in the ordinary refinery it is the phosphorus which is next or perhaps simultaneously attacked, whilst in the Bessemer process the phosphorus remains unchanged. Experiments made at the Weardale Iron Company's Works with Cleveland pig iron in the Bessemer converter, showed that a pig iron containing C 3·60, Si 1·76, S 0·175 and P 1·64 respectively, lost, after a five minutes' blow, C. 8·61, per cent., Si 77·72, S 16·63, and gained, P 10·89 per cent. A pig iron containing C 3·452, Si 1·626, S 0·120, and P 1·423 per cent., after a nine minutes' blow, lost C 86·03 per cent., Si 98·8, and gained, S 0·005 and P 3·23 per cent. After a sixteen minutes' blow a pig iron containing C 3·48, Si 2·07, S 0·05, and P 1·46, lost C 98·56, Si 96·61, whilst the S remained unchanged, and the P gained 15·75 per cent. After a blow of twenty minutes, an iron containing C 3·87, Si 1·910, S 0·046, P 1·92, lost C 82·83, Si 99·63, and gained S 34·78 and P 15·78. The general conclusion is, that in refining, the loss per cent. on the original quantity present of Si is 90, C 10, S 30, P 50, whilst in the converter, according to the periods of blowing, the loss of Si is 77 to 99, C 8 to 99, whilst in S there is no change, and in P there is 10 to 16 per cent. of gain.

20 to 30 per cent. of fused ore and cinder was run into a converter before its charge of iron; after blowing, no phosphorus was found to have been removed. In another case the blast was continued until 25 per cent. of the iron was oxidised in the converter; the iron was quite liquid, but no phosphorus was removed.

When molten pig iron was poured slowly through a column of fused oxide of iron, 44·68 per cent. of the P was removed. There seems reason for believing that the high temperature of the metal in the Bessemer converter inverts this action between oxide of iron and phosphorus.

Carbon is that element which makes pig iron fusible at comparatively low temperatures, and, except in the converter, carbon is more tenaciously retained than Si, S, or P. If the carbon is removed too rapidly, the phosphorus may not be removed. A portion of Clarence pig, from which nearly all the carbon had been burnt off, was transferred from the converter to a "fettled" puddling furnace, and was ready for balling in five minutes, giving little time for the oxidation of the phosphorus. Another portion was transferred to a furnace charged with melted oxide of iron. In the first case the phosphorus was reduced from 1·46 per cent. in the original iron to 0·74 per cent., in the second case from 1·46 to 0·54 per cent. Experience shows that the impurities are more easily removed when the pig is melted before charging the puddling furnace. Bar iron puddled cold contained 0·597 per cent. of P; puddled hot, 0·299. In another case 0·592 and 0·209 per cent. of P respectively were obtained.

Analyses by Proctor show that in the Danks' furnace, neglecting the small quantity of sulphur, the silicon is mainly removed during the melting of the charge; phosphorus coming next in amount, and lastly carbon. Before balling, the phosphorus and carbon have lost equal amounts (per cent. of originals), and from this point the phosphorus remains unchanged. In puddling, the heat required for finishing the process may approach that at which the phosphorus is no longer oxidised. In portions the temperature may be so high that the iron takes up phosphorus from the slag, for puddled bar sometimes contains more phosphorus than the same iron at an earlier stage. Iron free from phosphorus in a bath of slag containing phosphorus, in a Siemens-Martin furnace, was found to take up phosphorus towards the end of the heat. Machine puddling removes phosphorus more completely than hand puddling, and the iron produced is more uniform in quality. J. T.

Method of imparting Sonorousness to Soft Metallic Alloys. By B. SILLIMAN (*Dingl. polyt. J.*, ccxxv, 268—270).—B. Silliman, of Newhaven (Conn.), has invented a method of making soft metal alloys, such as pewter, Britannia metal, &c., sonorous.

A capacious oil or paraffin bath is heated to a temperature from 5° to 5·5° degrees below the melting point of the alloy to be treated. The exact point is determined in each case by heating the bath until a sample alloy, freely suspended, just begins to be scratched by a wire which has a slightly higher melting point. Small and thin articles are then immersed for from 15 to 30 seconds; larger articles, such as urns, remain in a minute or more. Careful handling is necessary to prevent distortion.

It is immaterial whether the articles be cooled quickly or slowly, and the process may be repeated if necessary; but it is essential that each article be heated uniformly, or the parts not sufficiently heated will have a prejudicial effect on the tone. Although the alloy may lose something of the compactness imparted to it by rolling, pressing, &c., yet it does not become porous, whilst its hardness and stiffness are increased. Alloys thus treated can be soldered, plated, &c., but cannot be hammered, pressed, &c., without injuring their sounding qualities. J. T.

Crystallisation of Metallic Oxides from Glass. By PAUL EBELL (*Dingl. polyt. J.*, ccxxv, 70—78, and 168—175).—In former communications (1874, ccxiii, 53, and 1876, ccxx, 64), the author has shown by a number of examples, that glass in the molten state is a powerful solvent for many bodies, which in consequence play an important part in glass manufacture. The action of the metals silver, gold, and copper, with formation of aventurine and hæmatinone, was noticed, and the results of fusion of glass with alumina, oxide of iron, manganese, chromium, zinc, were also given. In the present communication he deals with the action of silica, lime, baryta, sulphate of sodium, phosphate of calcium, cryolite and sulphides.

1. *Behaviour of Glass fused with excess of Silica.*—In all the experiments the glass was formed by fusing a mixture called Hautefeuille's mixture, of the following composition. Sand, 150 parts; chalk, 35·5; calcined soda, 80; potash, 14·0; nitre, 20. This Hautefeuille mixture

was fused with 42·86 per cent., 66·67 per cent., and 118·67 per cent. of silica respectively, and the results were as follows:—The first two could be fused at high temperatures, but gave no signs of crystallisation in the interior of the glass, even when very slowly cooled. The third, though it could be fused, was less fluid than the others. Quickly cooled specimens were transparent, but exhibited a shade of green. Specimens slowly cooled showed long six-sided crystalline forms, of milky whiteness, and resembling the tridymite of blast furnaces.

2. *Behaviour of Glass with excess of Lime.*—The following mixtures were fused:—(*a*) 100 parts of Hautefeuille mixture and 100 parts lime. (*b*) 100 parts of Hautefeuille and 200 of lime. Both *a* and *b* gave at high temperatures a perfectly clear glass; *a*, when rapidly cooled, gave a transparent glass. When slowly cooled, the result had a stony appearance. Microscopic examination showed white long needle-like crystals; *b* was very similar in its behaviour, but the crystals were more numerous.

3. *Behaviour of Calcium Phosphate with Glass.*—Phosphate has long been used for giving a milky appearance to glass. The addition of 10 to 20 per cent. of burnt bones causes the glass to assume the form of milk-glass or opal glass. If quickly cooled the glass is transparent, but on gentle warming the whole becomes suddenly white. An experiment made by melting 100 parts of glass with 30 parts of burnt bones showed that the bone-ash is dissolved with difficulty, on account of its lightness. In 1863 (*Dingl.*, clxvii, 27) Schür proposed to substitute guano for bone-ash, and with good results. The author thinks, however, that a compound of definite composition would be better, and prepares a phosphate by precipitating an ammoniacal solution of calcium chloride with sodium phosphate. A mixture of 300 parts of broken white-glass with 30 of this calcium phosphate, melts easily. Quickly cooled specimens are colourless and transparent, but become milk-white on warming. Slowly cooled specimens are white, but the particles in the glass are larger than in the other case.

Another mixture of 300 parts of broken pieces of white glass with 60 of calcium phosphate was melted and part poured out. This of course cooled suddenly, and when gently warmed became milk-white as in the former case. The crystals in the glass were very small. The remainder in the crucible cooled very slowly, and had quite a different appearance. Though it was milk-white, the cloudiness was less dense. The crystals were large and lay in a clear glass, and were visible to the naked eye. An experiment was made to discover the nature of these crystals by treating a thin section with hydrochloric acid. The crystals disappeared, and the author therefore considers the crystals to be calcium phosphate. Another fact noticed during these experiments was that calcium phosphate, though generally reducible with difficulty, can, in the presence of the molten glass, be easily reduced to calcium phosphide by coal, the result being to colour the glass very black.

4. *Fusion of Cryolite with Glass.*—In the manufacture of white or milk-glass cryolite has often been substituted for bone-ash, and with good results. Benrath in 1869 (*Dingl. polyt. J.*, cxcii, 239)

analysed the glass and found SiO_2, 70·01; Al_2O_3, 10·78, and Na_2O, 19·21. As he found no fluorine, he thought the small crystals which made the glass opaque must be Al_2O_3. Richters (1869, cxci, 301) found much fluorine, and considered it essential in the production of the milky appearance.

It has been already shown that a large quantity of alumina can be dissolved in the glass without affecting its transparency. Cryolite and sand in proportion of 1 to 2 were fused. Fluoride of silicon escaped during the fusion, and the product when cooled rapidly was a transparent colourless glass. On warming it became opaque. The mass left in crucible to cool slowly was less opaque, the crystals, as in case of calcium phosphate of lime, being larger and more scattered in a clear base. On analysis the glass gave 1·74 per cent. of fluorine. On re-melting this opaque glass with silica to drive off all the fluorine, the resulting glass gave no appearance of milkiness. This proves that fluorine is necessary to the formation of these crystals.

It cannot be in the form of fluor spar, however, as calcium fluoride has long been employed in glass manufacture, and yet this milkiness has not been observed. It cannot be in the form of sodium fluoride, as the crystals are insoluble. The author therefore thinks that it must be some fluoride of aluminium, and he supports this belief by the following experiment: 100 parts of broken lime glass and 10 parts of silico-fluoride of sodium were melted together. The product had a greenish appearance, but the glass would not run. This proves that neither sodium nor lime forms part of the crystals.

5. *Fusion of Sulphates with Glass.*—Pelouze (1865, *Dingl. polyt. J.*, clxxviii, 134, and 1867, clxxxiv, 310) has shown that glass can contain 3 per cent. of sodium sulphate. The author found 3·6 per cent. of this substance in some experiments he made.

6. *Fusion with Sulphides.*—Sulphides of sodium and calcium give an intense red colour, which shades off into brown. The sulphides are usually obtained in the glass manufacture by reduction with coal, during the fusion of glass of sulphates. When fused with sulphides, the red glass on quickly cooling is transparent, but by slowly cooling, crystals large and small are found in the glass. Instead of adding a sulphide, sulphur alone can be added if the glass be a sodium or potassium glass. The resulting glass is however browner than in the former case.

Many experiments showed that when free silica is present, the glass remains colourless, although sulphur or sulphides be added. This proves that to colour a glass, more base must be present than the silica can unite with. In this case the sulphur can form a sulphide, and the glass is coloured. As a result of several experiments, a neutral glass which colours with sulphides has the following composition: 1 part of base to 2·5 parts of silica, or $2RO + 5SiO_2$.. When this proportion of silica is exceeded, the glass does not colour; when it is below this, the colour becomes very intense. S.

Toughened Glass. By BOWRÉE (*Dingl polyt. J.*, ccxxv, 360—365).—The author passed some time at the glass works at Choisy-le-Roi, and had therefore had the opportunity of carefully examining the process of toughening glass (1875, ccxv, 186—381; ccxvi, 75; ccxviii, 181) in its details.

The glass, after receiving its form, is cooled in a bath of certain temperature, defined by experiment, and varying 1st with the heat to which the glass vessel or object is heated before immersion; 2nd, with the size and thickness of the vessel or object, and with the chemical composition of the glass. The chemical composition affects the amount of softening, and therefore the degree to which the glass can be heated, and so indirectly the temperature of the bath. The author experimented with a glass of 300 parts of sand, 100 of potash and soda, and 50 of red lead. This could be easily toughened, and so can all crystal-glass, in a bath of fat at temperatures varying from 60° to 138°; common glass in a mixture of oil and fat between 150° and 315°. The amount of soda and potash has a great influence on the power of toughening.

The thicker objects require more heating, and a hotter bath.

The mixture of the bath is also a point of great importance. All substances have not the same value in this respect. Water always makes the glass brittle. The best results are obtained with *pure* fats and oils. With crystal-glass and low temperatures, fat is the best; with higher temperatures oil and fat are employed.

The objects must be heated *uniformly*, or the results will be unfavourable.

The objects must be made of *homogeneous* glass, and heated *uniformly*.

The oil or fat baths must be easily movable, and at the same time large enough to contain several objects at the same time. A small tramway on which the bath may run is suggested. There are many points of the utmost importance in the manipulation of the glass while being immersed that only long practice can teach; and yet the success of the operation depends on them.

After the objects are placed in the fat-bath, the bath is placed in a room for four or five hours at the melting-point of the fat. After this, the glass is cleansed by caustic soda. When oil is used, the glass is cooled more slowly, as the bath is kept hot for a longer period.

The cost of toughening is—

For drinking glasses of all kinds,	·21 to ·33*d*.	
„ lamp-cylinders,	·30*d*.	
„ lamp-globes,	·50*d*.	S.

Analyses of Glass. By F. PRIMKE (*Dingl. polyt. J.*, cxxv, 174). I. Glass bell-jar of a Thomson's electrometer which showed great power of insulation. II. Glass of very similar composition used for optical purposes, and analysed byBerthier:—

	SiO_2.	K^2O.	Na_2O.	PbO.	CaO.	MgO.	Fe_2O_3	MnO.	
1.	58·450	9·236	3·745	28·019	0·064	0·054	0·474	—	= 100·042
II.	59·2	9·0	—	28·2	—	—	0·4	1·0	= 97·8

Impurities neglected, the composition is as follows:—

SiO_2.	K_2O.	Na_2O.	PbO.	
58·77	9·28	3·77	28·18 = 100	S.

General and Physical Chemistry.

Existence of Oxygen in the Sun, and a New Theory of the Solar Spectrum. By H. Draper (*Compt. rend.*, lxxxv, 613—614).—Uniting all the conditions for obtaining the best results, the author photographed simultaneously the spectrum of the sun and that of oxygen rendered incandescent by the sparks of a Ruhmkorff coil. The photographs showed that the lines of the oxygen spectrum exactly coincided in position and relative intensity with certain bright lines in the solar spectrum, thus proving the existence of oxygen in the sun. The solar spectrum must therefore no longer be regarded as a continuous spectrum with no other than the absorption lines produced by metallic vapours; it must be admitted that it also contains superimposed lines and bands brighter than the field of the continuous spectrum. These brighter lines may reveal the existence of other non-metallic elements, and perhaps some of the so-called dark lines ought to be regarded as merely intervals between the brighter lines.

R. R.

Transverse Absorption of Light. By W. Akroyd (*Chem. News*, xxxvi, 159).—In a former paper (see this *Journal*, i, 1877, 571), the author has pointed out the difference between *structural* and *transverse* absorption. In the present paper he describes a new method of observation. The absorbing liquid is placed in a small glass trough, the ends of which are made of thin microscopic glass; the light passes at right angles to the absorbing medium, and dispersion is eliminated; the results are quantitative. The *principle of constancy of absorption* is laid down, viz., a constant number of molecules of a substance when similarly aggregated produces the same amount of transverse absorption. It is shown experimentally that a solution of potassium dichromate gives the same amount of absorption as a plate of the solid itself containing the same amount of dichrome as was contained in the solution. The size of the particles producing isolated absorption-bands is approximately determined for a few substances. The following numbers are given:—

	Incipient absorption.	Width of molecular aggregate in mm.
Potassium permanganate....	3 bands	80
Methylaniline violet	1 band	63
Magenta..................	1 „	47
Iodine green	1 „	480

The smaller the size of the particles in a given thickness of solid, the more readily do short wave radiations appear to be absorbed.

M. M. P. M.

Conductivity of Electrolytes. By A. F. Berggren (*Ann. Chim. Phys.* [2], i, 499—510).—The author used Pallzow's method, described in the *Berlin Monatsbericht* (1868, p. 486). He found, however, that this method was applicable only to such fluids as did not react with the amalgamated zinc plates. After explaining in considerable detail the method employed, the author gives his results in a tabular form, the substances with which he experimented being normal and acid potassium sulphates, normal sodium sulphate, magnesium sulphate, normal ammonium sulphate, and sodium chloride. The results of these experiments are represented graphically in plate iii, fig. 4 of the volume.

The conductivity appears continuously either to increase or diminish with an increasing concentration of the solution in the different cases. In the case of potassium sulphate the conductivity appears to increase. Kohlrausch and Grotrian have found that in the case of potassium chloride, the relation between the conductivity and the percentage of salt in solution may be expressed by a straight line. The conductivity of sodium sulphate seems to increase less rapidily with an increased percentage of salt in solution than in the case of potassium sulphate. In ammonium sulphate the conductivity also increases with the salt percentage, but appears to approach a maximum, as with a further increase in density of the solution no further increase in conductivity can be observed.

The solution of magnesium sulphate which proves the best conductor contains about 16 per cent. of salt, and the conductivity was measured at about 8° C. Acid potassium sulphate did not yield such regular results as the other salts. This the author conjectures may be due to impurities. It is, however, a better conductor than the normal salt.

According to their conductivity, the sulphates may be arranged in the following order:—$(NH_4)_2SO_4$, $KHSO_4$, K_2SO_4, Na_2SO_4, and $MgSO_4$. Kohlrausch and Grotrian have found the following order in the conductivity of the chlorides of the alkaline earths and alkalis:—$(NH_4)Cl$, KCl, $NaCl$, $LiCl$, $CaCl_2$, $SrCl_2$, $CaCl_2$, and $MgCl_2$. Certain analogies, therefore, would appear to exist between the chlorides just mentioned and their corresponding sulphates.

Among these salts, the solutions of which have a relatively high conductivity the ammonium salts rank highest. Kohlrausch and Grotrian found a solution of ammonium chloride, the conductivity of which was almost half that of the best acid conductors. Wiedemann also has found that ammonium nitrate has a very high conductivity. The author's experiments show that ammonium sulphate has a conductivity considerably higher than that of any of the other sulphates investigated.

The following table contains some determinations of the conductivity of solutions of potassium, sodium, ammonium, and magnesium chlorides compared with that of their corresponding sulphates in solution, the former being taken from Kohlrausch and Grotrian:—

Per cent.	*t*.	Substance.	10^8L.	Substance.	10^8L.
5	8	KCl	520	R_2SO_4	335
5	7	NaCl	486	Na_2SO_4	278
5	8	NH_4Cl	696	$(NH_4)_2SO_4$	384
10	8	”	1365	”	732
15	7	”	1980	”	1036
20	6	”	2547	”	1244
5	8	$MgCl_2$	503	$MgSO_4$	186
10	8	”	827	”	282

From this it may be easily seen that the alkaline chlorides possess a higher conductivity than the corresponding sulphates. J. M. T.

Determination of the Electric Conductivity of certain Liquids with a Constant Current. By J. TOLLINGER (*Ann. Chem. Phys.* [2], ii, 510—516).—The object of the author in these experiments has been, not so much to reinvestigate the conductivity of liquids already determined, as to test by constant currents the values found by Kohlrausch and Grotrian with varying currents.

As difficulties and objections have been found to the use of troughs and straight glass tubes in the experiments, the author employs a U-tube, and to obtain a more constant polarisation he uses as electrodes spirals of platinum wire, which have the further advantage of allowing any gas generated to escape readily. The column of liquid to be tested was introduced, together with a rheostat, into one branch of a Wheatstone's bridge, whilst a similar tube with equal electrodes filled with the same liquid, as well as a rheostat, was placed in the other branch, in order to eliminate small changes in polarisation due to changes of temperature and irregularities of the currents. The whole arrangement is shown in plate iv, fig. 1, of the volume.

During the experiment the electrodes of the second tube, as well as the resistance selected, remain constant, while in the other branch of the bridge the electrodes are lengthened and shortened. To preserve a constant temperature, a large water-bath was used, into which the whole apparatus was placed. With the exception of sulphuric acid, the liquids investigated by Kohlrausch were employed. In the following table, so far as possible, Kohlrausch's results are compared with those of the author. Any differences between them may possibly be explained by slight differences in the nature of the liquids, arising from impurities.

1	2	3	4	5	6	7	8	9	10	11	12
Substance in solution.	Density.	Temperature.	Percentage of salt in 100.	Length of the fluid column.	Resistance of the same.	Temperature.	Conductivity k.				Difference between constant and varying current in percentages.
							With constant current at the temperatures:		With varying current at 18° according to:		
	Δ	$t\ \Delta$	p.	l M.	w.	$t°$	$t°$	18°	Tollinger.	Kohlrausch	
H_2SO_4.	1·8364	17·5	94·5	0·1500	107·2	16·53	943	983	..	980	+ 0·3
,, .	1·8286	18·3	92·5	0·1500	99·22	17·52	1018	1033	..	1030	+ 0·3
,, .	1·7787	18·1	84·6	0·1500	120·87	15·30	836	927	..	915	+ 1·3
,, .	1·2208	17·9	30·0	0·3000	28·96	18·33	6978	6941	..	6912	+ 0·4
$MgSO_4$.	1·1845	18·2	17·0	0·1490	217·08	18·14	461	461	457	451	+ 0·9
$ZnSO_4$.	1·2811	18·2	23·1	0·1490	213·30	18·74	471	462	460	452	+ 0·5
$CuSO_4$.	1·1681	18·4	15·1	0·1490	245·00	19·08	410	400	396	..	+ 1·0
$KHSO_4$	1·072	17·1	10·0	0·2990	140·35	18·30	1440	1436	1434	..	+ 0·1
K_2CO_3.	1·3483	18·1	34·0	0·2990	96.99	17·55	2078	2100	2086	2121	+ 0·7
LiCl ..	1·013	17·3	2·5	0·1490	255·47	18·80	393	386	383	..	+ 0·8
HNO_3.	1·1862	17·9	29·7	0·2990	27·96	16·48	7206	7362	7317	7330	+ 0·6
HCl...	1·0912	18·0	18·3	0·2990	28·87	16·17	6979	7182	7143	7174	+ 0·5

From these results it may be seen that the values found with constant and with induction currents do not differ materially.

J. M. T.

Specific Inductive Capacity. By V. NEYRENEUF (*Compt. rend.*, lxxxv, 547).—The author's experiments relate to the energy of the sparks which pass between the plates of a condenser when dielectrics of different kinds and thicknesses are interposed. The results confirm the established laws of electric induction. R. R.

Thermoelectric Temperature Determinations. By ROSENTHAL and MÖLLER (*Chem. Centr.*, 1877, 241).—The authors have applied a thermopile of copper and iron to the determination of ground temperatures for hygienic purposes. M. M. P. M.

Specific Heat of Water according to the Investigations of W. Munchhaüsen. By A. WÜLLNER (*Ann. Chem. Phys.* [2], ii, 592—605).—The author alludes fully to experiments by Pfaundler and Platter, Hirn, Jamin and Amaury, Hess and Person, which do not quite agree with those of Regnault as to the equation for the specific heat of water between 0° and 100°. These differences between the various experimenters have led the author to institute a new series of investigations, the experimental part of which has been carried out by Munchhaüsen. A full description of the method employed and tables of the results found are given.

The author regrets that Munchhaüsen was not able to continue his experiments between 70° and 100°, but says that the experiments between 17 and 70° suffice to indicate the direction taken by the specific heat between the latter temperatures.

From the numbers obtained, the author deduces the following formula for the specific heat at t.

$$k = 1 + 0{\cdot}00030192\,t.$$

A calculation of the observations with this value for the constant, gives the mean error of experiment as ·0016; therefore, the probable error of ·00108. For comparison of the observations and calculations, Series II and VI are given.

Series II.			Series VI.		
Calculated.	Observed.	Δ	Calculated.	Observed.	Δ
1·0036	1·0019	+ 17	1·0070	1·0083	− 13
„ 36	„ 33	+ 3	„ 65	„ 58	+ 7
„ 32	„ 59	− 27	„ 62	„ 54	+ 8
„ 36	„ 31	+ 5	„ 64	„ 60	+ 4
„ 36	„ 46	− 10	„ 66	„ 89	− 23
„ 37	„ 57	− 20	„ 67	„ 88	− 21
„ 37	„ 24	+ 13	„ 66	„ 35	+ 31
„ 38	„ 30	+ 8	„ 64	„ 75	− 11
„ 38	„ 41	− 3			
„ 39	„ 48	− 9			
„ 40	„ 25	+ 15			

From these it may be seen that the differences are of the same order in both series, so that the equation fully represents the results of experiment. The uncertainty of the value of the coefficient of temperature as given by the probable error is 0·0000099; so that the specific heat at t lies between

$$k = 1 + 0{\cdot}0002920\,t \text{ and}$$
$$k = 1 + 0{\cdot}0003118\,t.$$

The author then does away with the objection that a perceptible loss of heat might be caused by the passage of the water added to the calorimeter, through the air, his arguments being based on the experiments of Dulong on the rate of cooling of water in air.

The author concludes that between 0 and 70°, or if it be permitted to go beyond actual experiment, between 0 and 100° also, the results obtained show that the specific heat increases more rapidly than Regnault's numbers, but much more slowly than those of Jamin and Amaury; thus, k, according to the several experimenters, is as follows:—

	Wüllner.	Regnault.	Jamin.
At 20°	1·0060	1·0012	1·0235
„ 40	1·0121	1·0030	1·0459
„ 60	1·0181	1·0056	1·0703
„ 80	1·0241	1·0089	1·0957
„ 100	1·0302	1·0130	1·1220

According to the equation used by Jamin and Amaury, the increase in the specific heat would be about fourfold, and in the case of Regnault's, little less than one-half that found by the author at 100°.

J. M. T.

Note by the Abstractor.—It is difficult to give an adequate idea of the author's argument without a translation of the first part of his paper and the tables *in extenso*, which would be beyond the limits of this *Journal*.

Apparatus for Measuring the Heat of Vaporisation of Liquids. By M. Berthelot (*Compt. rend.*, lxxxv, 646—648).—The liquid is distilled from a flask-shaped glass vessel, the neck of which is, however, sealed at the top, and near to this internally is the open extremity of a glass tube, which traverses the centre of the vessel, passing out through the bottom. This tube is continued downwards from the bottom of the vessel for a short distance, and its lower extremity is adapted to a worm-tube wholly immersed in the water of the calorimeter. The apparatus is figured in the paper, which also describes the mode of operating. R. R.

Determination of the Heat of Fusion. By M. Berthelot (*Compt. rend.*, lxxxv, 648—651).—In this paper the author shows the influence which differences in the physical states of a body may have in determinations of its heat of fusion. The states referred to are not isomeric modifications of the substances, but change, like those induced by the variable plasticity of resinous bodies. Very different values are obtained for the heat of fusion of chloral hydrate when the sample has been recently melted and then solidified, since this substance will even for days continue to retain some portion of its heat of fusion, and several months will be required for its return to a determinate thermal condition. R. R.

Specific Heat and Latent Heat of Fusion of Platinum. By J. Violle (*Compt. rend.*, lxxxv, 543—546).—The paper describes the method adopted by the author for determinations of the specific heat of platinum at high temperatures. The results lead to the following formula for the mean specific heat of platinum between 0° and t°:—$C_0^t = 0{\cdot}0317 + 0{\cdot}000006t$, the superior limit being 1200°. Between the same limits the true specific heat at t° is represented by $\gamma_t = 0{\cdot}317 + 0{\cdot}000012t$. Assuming these formulæ to represent the specific heat of platinum up to the melting point, the author applies them to the experimental results obtained with the fused metal, and arrives at 1779° as the melting point of platinum, and 27·18 as its latent heat of fusion. The data which are supplied by the author's experiments permit platinum to be used in determinations of high-temperature melting points and specific heats of other substances. He has in this way obtained 954° as the melting point of pure silver. R. R.

Contributions to Chemical Statics. By Ernst Brücke (*Wien. Akad. Ber.*, lxxv, 507—222).—The author has studied the influence of temperature, dilution, addition of acids, and condition of molecular aggregation on the coloured solution produced by adding salicylic acid to ferric chloride. The violet tint of iron salicylate is developed only in slightly acid solutions; on cautiously neutralizing, a Burgundy wine tint is first developed, and then the solution becomes yellow or colourless. On boiling a solution prepared by adding salicylic acid to ferric chloride until no alteration is produced by adding to the coloured liquid either a little ferric chloride or a little salicylic acid, the tint disappears to a greater or lesser extent, but is reproduced slowly on cooling and standing, so that after some days the colour is the same as before heating. Analogous results are obtained if the coloured liquid be acidified with small quantities of hydrochloric, phosphoric, or sulphuric acid before heating; the acid causes in the cold a greater or less lightening in tint according to the quantity added, complete decoloration ensuing after a certain amount is added. A dark-coloured solution, which has been partially lightened by addition of acid, is much less bleached on dilution with water than one of the same tint, but not containing acid; whilst a solution to which just enough acid has been added to destroy all the violet tint is rendered distinctly violet on adding distilled water. It is possible to use ferric salicylate as an indicator in titrating sulphuric, nitric, and hydrochloric acids, but it does not answer with organic acids such as oxalic, tartaric, acetic, &c. These acids act differently from the mineral acids so far as modifying the colour is concerned; thus, little or no effect is produced on heating a solution lightened in tint by oxalic acid, and but little violet is produced on diluting a solution just bleached by oxalic acid. Citric, tartaric, and acetic and succinic acids produce the same result as hydrochloric acid on heating (*i.e.*, the solution is more or less decolorised, the tint reappearing on cooling). A much larger quantity of acetic acid is, however, requisite than of hydrochloric acid, and so on with the others. Formic acid acts as oxalic acid, and not as acetic.

The colouring matter of ferric salicylate is not suspended solid matter; no settling takes place even on long standing; moreover, the coloured fluid is diffusible through bladders, &c. Attempts to prepare crystallised ferric salicylate did not succeed. C. R. A. W.

Observations on the Principle of Maximum Work, and on the Spontaneous Decomposition of Hydrated Barium Dioxide. By M. BERTHELOT (*Compt. rend.*, lxxxv, 880).—The following observations ilustrate the tendency of chemical systems to assume that particular arangement which coincides with the evolution of the maximum amount of heat in their formation. Barium dioxide, the subject of these experiments, is stable in the anhydrous state, but decomposes spontaneously when hydrated:—A specimen of the anhydrous dioxide, prepared in January, 1874, contained at that time 9·4 per cent. of oxygen more than required for barium monoxide; in November, 1877, it contained 92 per cent.

The hydrated dioxide, however, decomposes more easily, especially in presence of excess of water, with formation of the ordinary hydrate, $BaO.10H_2O$. Some crystallised hydrated barium dioxide contained in January 1874, eight per cent. available oxygen; some of it was mixed with half its weight of water, and placed in three flasks securely stoppered. In November 1877, the first and third flasks contained only 6·5 per cent. available oxygen, and the second only 6·1 per cent.

The formation of crystallised barium hydrate (which contains $10H_2O$) tends to dehydrate the neighbouring portions of hydrated dioxide, and, if excess of water be not present, the anhydrous dioxide thus formed decomposes very slowly. A portion of the same specimen of dioxide, kept for the same length of time under a layer of water, contained only 0·28 per cent. of available oxygen.

The thermal phenomena accompanying these reactions are as follows:—

The decomposition of anhydrous barium dioxide absorbs heat: $BaO_2 = BaO + O$ absorbs 6·05, so that this decomposition requires the aid of heat. The transformation of barium dioxide into barium monohydrate and free oxygen disengages heat: $BaO_2 + H_2O = BaH_2O_2 + O$ evolves 2·76 kil.-degrees (liquid water); + 2·0 (solid water). The same for the higher hydrates: $BaO_2.7H_2O + 3H_2O = BaO.10H_2O + O$ gives + 5·3 (liquid water); + 3·2 (solid water).

Pure hydrated barium dioxide changes more slowly, since each molecule of hydrated barium oxide requires for its formation a certain number of molecules of water from the neighbouring dioxide; $10(BaO_{2}.{}_{7}H_2O) = 7(BaO.10H_2O) + 7O + 3BaO_2$ disengages + 9·5.

C. W. W.

Influence of Polymerisation on Chemical Compounds. By J. LÖWENTHAL (*Chem. Centr.*, 1877, 193).—This theory is intended to explain why an element is in some cases easily removed from a compound, and in others is not removable without destroying the whole compound; the cause of isomerism; why an element unites with one element in preference to another; why an element sometimes combines and sometimes refuses to combine; and, lastly, reciprocal action, *i.e.*, why *a* removes *c* from *b c* in some cases, and in others *b* from *a c*. The theory supposes the atomicity of elements to depend on the polymerisation of the atoms; this influences also their force of combination, and accounts for allotropic conditions. W. R.

Molecular Changes. By H. J. v. JONSTORFF (*Chem. Centr.*, 1877, 321).—Small crystals of iodine, after eight years' keeping, had considerably increased in size. Amorphous phosphorus was partially changed into the crystalline variety, after nine years' keeping.

M. M. P. M.

Action of Anhydrous Acids upon Anhydrous Bases. By J. BÉCHAMP (*Compt. rend.*, lxxxv, 799).—Anhydrous lime, projected into anhydrous boric acid in a state of fusion, yields borate of lime. Anhydrous acetic acid acts upon anhydrous lime at 133°, forming calcium acetate; the product was dissolved in water and crystallised. The same anhydrous acid combines with anhydrous baryta at 100°. Anhydrous butyric and caproic acids combine with anhydrous lime at 120°; the theoretical yield of salt was almost fully realised. Anhydrous butyric and acetic acids combine with anhydrous ethylic oxide; the prolonged action of heat is necessary.

The same anhydrous acids unite directly with ethylene oxide.

These facts raise a question as to the correctness of the term "anhydride," now generally applied to these bodies by chemists who question their acid character. M. M. P. M.

Action of Animal Charcoal on Salts. By LEO. LIEBERMANN (*Wien. Acad. Ber.*, lxxiv, 331—344).—Having observed that on filtering through animal charcoal a neutral aqueous solution of the barium salt of the acid formed by oxidising glycerin with dilute chromic acid, the filtrate was strongly acid, and that water filtered through the same charcoal came through quite free from acidity, the author concluded that animal charcoal has the power of decomposing that salt and retaining the basic constituent: similarly barium formate was decomposed, the filtrate containing free formic acid capable of being distilled off. Somewhat analogous observations as to the retention by animal charcoal of certain substances have been made by Heumann, Chevallier, Weppen, and also Graham and Hofmann (strychnine), the action being ascribed in some of these instances to calcareous salts, &c., present in the charcoal. The author finds that a large number of salts are acted on by animal charcoal, some being wholly retained, and others decomposed, and the base retained to a greater or lesser extent, the action taking place with charcoal freed from earthy matters by treating it with hydrochloric acid and washing with water till the washings were free from chlorine. Horn- and blood-charcoal are the most active varieties, bone-charcoal also possessing the power to a large extent; wood-charcoal and coke are not efficacious in decomposing salts. To obtain numerical values, the purified charcoal was placed in pieces of combustion-tube 50 c.m. long, plugged at one end with cotton-wool, so as to fill the tube to a depth of 20—30 c.m., and the liquids to be examined were made to percolate through the mass: in this way the amount of substance contained in the percolate per c.c. could readily be compared with that in the original solution.

With barium formate, sodium and lead acetates, calcium glycollate, zinc lactate, ammonium oxalate, and potassium sodium tartrate, the basic constituents are retained to a greater extent than the acids, so that the percolates are distinctly acid. Potassium urate, sodium carbolate and benzoate, calcium benzoate, oxybenzoate, and paroxy-benzoate, barium benzoate, acid solutions of sodium salicylate, and calcium hippurate, were wholly retained: apparently the salts were decomposed, as on shaking with ether the charcoal through which calcium benzoate had passed, free benzoic acid was dissolved out. Morphine acetate is at first wholly retained; but on washing the charcoal subsequently with distilled water, free acetic acid is obtained; an analogous result is obtained with caffeine citrate. Strychnine nitrate, atropine sulphate, and quinine sulphate formed no free acid; sodium chloride, nitrate, and sulphate, and potassium chloride, iodide, bromide, cyanide, thiocyanate, nitrate, and sulphate also were not decomposed, but were partially retained; whilst sodium borate (alkaline), trisodium phosphate (strongly alkaline), and disodium-hydrogen phosphate (almost neutral) were decomposed, so that the percolates were at first neutral and subsequently acid. Calcium chloride and barium chloride and nitrate were not decomposed, but were retained to a considerable extent; whilst ferrous sulphate, copper sulphate, and silver nitrate were largely retained, especially the latter, the percolates being more or less acid: mercuric chloride (acid) passed through neutral, the percolate containing no mercury.

Solutions of exactly equivalent strength of acetic acid and caustic potash were prepared and made to percolate through the charcoal tubes, as was also a neutral mixture of equal bulks of these two fluids; in two experiments the quantities of substance retained by the charcoal were: acetic acid, 52 and 70 per cent.; potash, 72 and 92 per cent.; neutral salt, 16 and 23 per cent., these latter amounts consisting of more potash than corresponded with the acetic acid retained, the remainder being in the acid filtrate. Analogous results were obtained with copper sulphate solution, about one-fourth of the substance being retained, this amount containing more copper than that corresponding with the sulphuric acid retained.

Solutions of lead acetates in absolute alcohol passed through animal charcoal gave percolates containing no free acid; the author did not succeed in finding any acetic ether in the percolate: an analogous negative result was obtained with sodium acetate and amylic alcohol. [Apparently, however, fractional distillation only was employed, no mention being made of tests by distilling off the alcoholic liquors and saponifying them by alkalis.]

In order to see if aqueous solutions of salts dissociate spontaneously, salt was dissolved in water and the solution distilled in a current of carbon dioxide; a very faintly acid distillate containing chlorine was obtained. Analogous results were also yielded by barium chloride, no barium being in the distillate (*i.e.*, no spirting having taken place).

No galvanic current could be detected in the charcoal during its action on salts, even with a most sensitive galvanometer.

C. R. A. W.

Inorganic Chemistry.

Combustion of Nitrogen: a Lecture-experiment. By H. KÄMMERER (*Deut. Chem. Ges. Ber.*, x, 1684).—The direct combustion of nitrogen may be demonstrated by plunging an ignited piece of magnesium ribbon, 30—40 c.c. long, into a two-litre flask full of air. After the experiment the presence of nitrogen tetroxide is recognisable by its odour, and by its peculiar colour after the magnesia has settled: or it may be rendered more apparent by shaking up in the flask a solution of potassium iodide acidulated with acetic acid, and adding starch-paste, whereupon the dark-blue colour of starch iodide is produced.

J. R.

Combustion of Zinc and Cadmium: Lecture-experiments. By FRIDERICH GRAMP (*Deut. Chem. Ges. Ber.*, x, 1684).—The combustion of zinc may be shown in a striking manner by compressing zinc-turnings into a loose bundle some 40 mm. long and 20 mm. in diameter, and holding one end of the bundle, by means of tongs, in a gas-flame. The turnings take fire almost instantly and burn with a large dull-green flame, giving off dense white fumes of oxide which speedily condenses in flocks about the room. Or a heap of zinc-turnings on an iron plate may be ignited by a gas-flame. After the combustion there remains on the plate a large quantity of zinc oxide of a deep yellow colour while hot.

Cadmium, heated in a small porcelain crucible over the blowpipe, readily takes fire and burns with a dull-red flame, emitting dense brown clouds of oxide. J. R.

Apparently Anomalous Decompositions effected by Carbonic Acid. By Fr. Mohr (*Liebig's Annalen*, clxxxv, 286—295).—The results detailed below were obtained by passing carbon dioxide, washed with sodium carbonate, into a flask containing solutions of the various substances experimented with, until no more of the gas was absorbed, all air having been first swept out of the flask.

Barium acetate (10 grams in 100 c.c. of water), when saturated with carbon dioxide, deposited barium carbonate weighing 0·887 gram = 0·678 gram of acetic acid displaced.

Calcium and strontium acetates gave no precipitate with carbon dioxide.

Zinc acetate (10 grams in 100 c.c. of water), when saturated with the gas, deposited a crystalline precipitate containing 0·018 gram of carbon dioxide. The filtered liquid became turbid when heated, owing to decomposition of zinc bicarbonate dissolved in it.

Lead acetate (10 grams in 100 c.c. of water) speedily became turbid and deposited 4·715 grams of lead carbonate. The free acetic acid in the liquid was found by titration to amount to 1·976 grams, so that 73·6 per cent. of the lead acetate employed was decomposed in the experiment.

In the preceding cases the action of carbon dioxide may be accounted for by the fact that insoluble carbonates are formed. But there are cases in which similar decompositions are effected, although no precipitate is formed.

Neutral potassium chromate (5 grams in 100 c.c. of water) rapidly absorbed an amount of carbon dioxide which, when afterwards expelled by boiling and absorbed by baryta-water, gave 2·765 grams of barium carbonate = 0·596 grams of carbon dioxide.

Borax (5 grams in 100 c.c. of water) absorbed a large quantity of carbon dioxide, remaining clear. The solution, after boiling, contained free boric acid and sodium carbonate.

Sodium phosphate (10 grams in 100 c.c. of water) absorbed 0·627 gram of carbon dioxide, which was completely expelled by boiling.

Microcosmic salt (10 grams in 100 c.c.) absorbed 0·631 gram of carbon dioxide.

Sodium acetate (10 grams in 100 c.c.) absorbed 0·240 gram of carbon dioxide.

Sodium and potassium tartrate in aqueous solution absorbed carbon dioxide, and deposited acid potassium tartrate. J. R.

Purification of Hydrogen. By Eug. Varenne and Em. Hebré (*Bull. Soc. Chim.* [2], xxviii, 523—524).—The gas is passed through a solution of 2 parts of potassium bichromate in 20 parts of water and

1 part of sulphuric acid, which acts as effectively as potassium permanganate recommended by Schöbig.

The gas must be washed with potash to free it from traces of acids. L. T. O'S.

Preparation of Iodic Acid. By W. STEVENSON (*Chem. News*, xxxvi, 201).—Dissolve 2 parts baryta in 4 parts boiling water, add gradually 3 parts iodine, and filter when the solution is neutral and colourless. The precipitated barium iodate may be decomposed with sulphuric acid, and the liquid, after filtration, evaporated in a vacuum; iodic acid is then obtained. The first filtrate containing barium iodide may be used for the preparation of hydriodic acid by decomposing with sulphuric acid. M. M. P. M.

Change of Colour in certain Double Iodides. By R. BÖTTGER (*Chem. Centr.*, 1877, p. 2).—This change of colour, first observed by Meusel, is illustrated by the author in the following manner:—By coating the outside of a beaker made of tin-plate with mercuric iodide and argentic iodide (with the aid of "Cowdie pine resin" varnish) and of a second beaker with mercuric iodide and cuprous iodide, and filling them with water of about 70° to 80°; the yellow colour of the former is converted into a deep orange, while the red colour of the latter is changed to a blackish-brown shade. By emptying the beakers very quickly and refilling them with water of ordinary temperature, the original colours are reproduced. This interesting change of colour may in this manner be repeated several times. D. B.

On some Thionates. By H. BAKER (*Chem. News*, xxxvi, 203).—*Barium Dithionate.*—Saturated solution boils at 102°. 1 part dissolves in 0·994 of water. Sp. gr. at 15·5° = 4·536.

Lead Dithionate.—1 part dissolves in 0·869 of water at 28·5°. Sp. gr. at 11° = 3·259.

Calcium Dithionate.—Sp. gr. at 11° = 2·176.

Nickel Dithionate.—1 part dissolves in 0·897 of water at 12°.

Magnesium Dithionate.—Oblique prisms. 1 part dissolves in 0·692 water at 17°.

Sodium Dithionate.—Sp. gr. at 11° = 2·175. Rhombic crystals, $\breve{a} : \bar{b} : c = 0{\cdot}9922 : 1{\cdot}0 : 0{\cdot}5981$. Forms occurring are ∞P, $\bar{P}\infty$, P, $\bar{P}\frac{1}{2}$, $\infty P\infty$. Type is long prismatic.

Silver Dithionate.—$\breve{a} : \bar{b} : c = 0{\cdot}9884 : 1{\cdot}0 : 0{\cdot}5811$. Forms are $\bar{P}\infty$, P, ∞P, $\bar{P}\frac{1}{2}$, $\infty\bar{P}\infty$, $\infty\breve{P}\infty$. Type very short prismatic.

Silver-sodium Dithionate.—$\breve{a} : \bar{b} : c = 0{\cdot}9813 : 1{\cdot}0 : 0{\cdot}5856$. Forms are $\bar{P}\infty$, P, $\infty P\infty$, ∞P, $\infty\bar{P}\infty$. Cleavage-plane = ∞P. Crystals are horizontally prismatic from development of dome.

Potassium Trithionate.—$\breve{a} : \bar{b} : c : = 0{\cdot}3586 : 1{\cdot}0 : 0{\cdot}4204$. Forms are ∞P, $\infty\breve{P}2$, $\infty\bar{P}\infty$, $\infty\breve{P}\infty$, $\breve{P}\infty$. The salt is prepared by acting on a saturated solution of potassium thiosulphate with SO_2. Sodium thiosulphate similarly treated undergoes no change.

M. M. P. M.

New Double Salts of Hydroxylamine. By W. MEYERINGH (*Deut. Chem. Ges. Ber.*, x, 1946).—Hydroxylamine sulphate combines with aluminic, chromic, and ferric sulphates to form the following double-salts, which correspond exactly in composition and crystalline form with the alums:—

$$(NH_2OH)_2H_2SO_4,\ Al_2(SO_4)_3\ .\ 24aq.;$$
$$(NH_2OH)_2H_2SO_4,\ Cr_2(SO_4)_3\ .\ 24aq.;$$
$$(NH_2OH)_2H_2SO_4,\ Fe_2(SO_4)_3\ .\ 24aq.$$

The author has also obtained a double sulphate of hydroxylamine and magnesium, crystallising in long needles of the formula—

$$MgSO_4(NH_2OH)_2H_2SO_46aq.$$

J. R.

Action of Neutral Sodium Phosphate on Insoluble Carbonates. By A. FREBAULT and A. DESTREM (*Bull. Soc. Chim.* [2], xxvii, 449—501).—The author confirms the views of Thénard, Soubeyran, and Lecanu, with regard to the action of calcium phosphate on sodium carbonate, which they explain thus:—$2CaH_4(PO_4)_2 + 2Na_2CO_3 = 2Na_2HPO_4 + Ca_2H_2(PO_4)_2 + 2CO_2 + 2H_2O$, and not, as generally represented in books, thus:—$CaH_4(PO_4)_2 + 2Na_2CO_3 2Na_2HPO_4 + CaCO_3 + H_2O + CO_2$, which reaction they show to be impossible, inasmuch as the action of sodium phosphate on calcium carbonate gives rise to sodium carbonate and calcium phosphate. L. T. O'S.

Silver-ultramarine. By KARL HEUMANN (*Deut. Chem. Ges. Ber.*, x, 1888—1889).—The author has isolated this compound, which is of a pure yellow colour. It is gradually blackened and decomposed by boiling with solutions of sodium monosulphide and hydrosulphide, but the sodium ultramarine cannot be regenerated in this way.

C. F. C.

Preparation of Pure Cuprous Chloride. By R. BÖTTGER (*Chem. Centr.*, 1877, p. 576).—An aqueous solution of cupric sulphate is saturated with sodium chloride, a small quantity of metallic copper, in the form of strips, is added, the liquid is boiled for 10 minutes, and is then filtered into cold water; cuprous chloride precipitates as a snow-white powder. M. M. P. M.

Double Salts of Cuprous Thiosulphate. By F. R. KESSEL (*Deut. Chem. Ges. Ber.*, x, 1677).—On mixing solutions of potassium thiosulphate and cupric sulphate, there is thrown down a yellow precipitate, to which Rammelsberg assigned the formula $K_2S_2O_3.Cu_2S_2O_3$. The corresponding sodium salt was afterwards examined by Lenz and Siewert, who found it to have the formula $Na_2S_2O_3.Cu_2S_2O_3.CuS$. The author's analyses of the sodium salt prepared at 10° agrees approximately with Siewert's result, but he finds that when prepared at lower temperatures the salt varies more and more in composition. Thus the atomic proportions of sodium, copper, and sulphur in the salt formed at various temperatures were the following:—

	Na.	Cu.	S.
At 10°	1 :	1·35 :	2·18
,, 0	1 :	1·35 :	1·95
,, – 10	1 :	0·25 :	0·866

or approximately 4Na : 4Cu : 4S or Na : Cu : S.

The salt, prepared at 10° is converted by cold hydrochloric acid into a white sandy powder, in which sodium, sulphur, and copper are present in the proportions—Na : S : 3Cu.

This substance is perfectly stable in dry air, but is decomposed by moisture, giving off sulphur dioxide and turning brown from separation of cupric sulphide. It dissolves in ammonia, forming a solution which turns blue slowly in the air. It is soluble in cold acetic acid: the solution gives with alkalis a red precipitate of cuprous oxide. Mineral acids decompose it, with separation of cupric sulphide. Strong soda-ley turns it red, separating cuprous oxide. When heated, in the dry state, it is resolved into cupric and cuprous sulphides, sodium sulphate, sulphur dioxide, and sulphur. The constitution of the substance is not yet made out.

In a subsequent paper (*Berichte*, x, 2000) the author corrects the preceding results, and gives for the proportional numbers of atoms in the two salts the following numbers:—

	Na.	Cu.	S.
Yellow salt................	4 :	1 :	4
White salt	3 :	1 :	3

the white salt being formed from the yellow by abstraction of 1 at. Na and 1 at. S. J. R.

Preparation of Iron Silicofluoride. By FR. STOLBA (*Chem. Centr.*, 1877, p. 385).—An aqueous solution of the salt containing a little free silicofluoric acid, is evaporated until a crust begins to form. Strong alcohol is then added so long as a precipitate is produced, the precipitated salt is collected on a funnel stopped with cotton wool, washed with strong alcohol (using the pump), and placed on a porcelain plate in a dry place. The salt as thus prepared is very stable. The corresponding salts of cobalt, nickel, and zinc may also be precipitated from aqueous solutions by addition of strong alcohol.

M. M. P. M.

Preparation of Platinum Black. By R. BÖTTGER (*Chem. Centr.*, 1877, p. 576).—By boiling platinic chloride solution with Rochelle salts, carbon dioxide is evolved and the whole of the platinum is precipitated in the finely divided state. M. M. P. M.

The Working-up of Uranium Residues from Phosphoric Acid Determinations. By F. STROHMER (*Dingl. polyt. J.*, ccxxv, 561—565).—After describing methods by Knop, Reichardt, Jani, and Gawalowsky, the author proposes to fuse the residues for half-an-hour with four parts of mixed sodium and potassium carbonates to which some charcoal has been added. An iron crucible is best, though a Hessian or porcelain one may be used. After treating with hot water and washing until free from soda, the residue is dissolved in hydrochloric acid containing a little nitric; and the iron and uranium are precipitated by ammonia, and separated by ammonium carbonate.

J. T.

Mineralogical Chemistry.

Analyses of Orthite, Vasite, Erdmannite, Tritomite, and Archenite. By N. Engström (*Deut. Chem. Ges. Ber.*, x, 1727).—The author's analyses of *orthite* from various localities lead to the formula, $2(2RO.SiO_2) + 3R_2O_3.4SiO_2$, with 1 or 2 aq. $Si_6(R_2)_3R_4H_2O_{26}$, is regarded as the true formula of undecomposed orthite.

Vasite was found to be merely decomposed orthite.

Erdmannite and *tritomite* both belong to the borates, containing 7—8 per cent. of boric anhydride.

Archenite from Ytterby contains tantalic and silicic acids in about equal quantities, and appears to be a decomposition-product of the tantalo-niobates found in the same locality. J. R.

Analysis of Periclase. By A. Cossa (*Deut. Chem. Ges. Ber.*, x, 1747).—The author found in periclase contained in predazzite from Monte Somma, 95·6 per cent. of magnesia and 4·4 per cent. of ferrous oxide. The density of the mineral was 3·642 at 12°.

Cossa obtained crystallised magnesia by fusing together magnesium sulphate and sodium chloride at a very high temperature for four hours in a platinum crucible, and allowing the mass to cool slowly. Somewhat larger crystals of a reddish colour were formed on adding a little ferrous sulphate to the mixture. J. R.

Chalkophanite, a New Mineral Species. By Moore (*Chem. Centr.*, 1877, p. 8).—In the calamine works of the Passaic Zinc Company at Sterling Hill, Ogdensberg, New Jersey, a deposit was found over the calamine ore, which includes more or less the decomposition-products of Franklinite and other manganiferous and zinciferous minerals. The material is fissured, and contains cavities which are filled up with a crystallised mineral; the crystals are rhombic, have a hardness of 2·5°; a specific gravity of 3·907, a metallic lustre, and a blue to iron-black colour. When the mineral is heated before the blowpipe, the pale-yellow bronze colour is converted into a copper-red, and the mass shows slight indications of melting, while the colour becomes darker and darker as the heating is continued. D. B.

Morphological Studies of Brookite. By A. Schrauf (*Jahrb. f. Min.*, 1877, 403-404).—The author confirms his previous and reiterated statements that brookite crystallises in the monosymmetrical, and not in the rhombic system, and further observations point to the complete isomorphism of wolframite and brookite, whilst the formula, TiO_2, for the latter is too simple. In the *Jahrb. f. Min.*, 1873, 754 (*Chem. Soc. J.*, 1873, 235), he described three types of brookite-crystals, giving their axial relations and the localities in which they were found. In the present communication the author points out that the well-known "dispersion" in the planes of the optical axes (although theoretically possible), is scarcely reconcilable with the optical symmetry of the rhombic system deduced from numerous observations. This dispersion, on the contrary, as "dispersion croissée," is one of the principal characteristics of the asymmetrical system. The theoretical explanation of this optical phenomenon becomes easier if brookite is considered to crystallise in the monosymmetrical system, for it is an established fact that monosymmetrical crystals with an apparent rhombic symmetry very commonly exhibit the characteristics of this system parallel to, or in the position of the axis of polarisation. From this the author contends that brookite and wolframite are isomorphous, whilst there can be no doubt that the three types of crystals of brookite are brought about by changes in chemical constitution. The few analyses which have been made of brookite are not sufficient to warrant any decided conclusions as to chemical changes in their constitution through "vicarious constituents," although iron and probably silica play, no doubt, an important part in these changes. The author determined the specific gravities of the three brookite types, and found them to be respectively as follows, viz.:—Type I. = 4·15; Type II. = 4·21; Type III. = 4·11. A qualitative examination of the substance driven off by ignition of brookite would be desirable, for if it be water, the analysis by Hermann leads to the formula, $H_6Fe_2Ti_{46}O_{98}$, for brookite; but other analyses of this mineral and the consideration of its isomorphism with wolframite, scarcely allow the assumption of a formula with eight valencies. Leaving out the iron and hydrogen as accidental constituents, and considering the trimorphism to be polymerism, the formula, Ti_2O_4, is arrived at for brookite. The isomorphism of brookite and wolframite compels a doubling of the molecular formula of the former, and the assumption of an equal valency in each of these bodies; the lowest possible valency being 16.

C. A. B.

Bismuthospherite. By A. Weisbach (*J. f. Min.*, 1877, 404—405).—The author instituted a further examination into the composition of the original specimens examined by Werner, and named by him *Arsen-wismuth*. These specimens came from the Neuglückspath vein at Neustädtel, near Schneeberg, and exhibited the so-called arsenwismuth in dull brown spherules and hemispherules, sometimes as large as a pea, and often enclosing a kernel of bismuth. The larger spherules have a concentric, undulating, shell-like structure, the smaller ones a fibrous structure, both being accompanied by quartz, and cobalt-speis, and attached to bitter-spar. Sometimes the exterior of the spherules is covered with a whitish, mealy deposit, the innermost shells exhibiting a light-yellow or light-brown colour, whilst the outer shells vary from a dark-brown to an almost black colour. The lustre increases in intensity as the mineral becomes darker in colour, but the fibrous structure becomes proportionately less well defined whilst the straw-yellow shells are the most distinctly fibrous and only exhibit a glimmering lustre. The various shell-structures gave the same streak, viz., yellowish-grey, and all of them dissolved in dilute hydrochloric acid with effervescence. No water was evolved on heating the mineral in a mattrass, but the mineral mass assumed a beautiful lemon-yellow colour. Hardness, 3. Spec. gr. 7·28 to 7·32. On analysis, the mineral proved to have the following percentage-composition, viz.:—

Bi_2O_3.	CO_2.	SiO_2.
88·58	8·97	0·28 = 97·83

from which the formula, Bi_2CO_5, is obtained, this formula requiring

91·34 Bi_2O_3 and 8·66 CO_2.

From this result it appears that the Arsen-wismuth of Werner is in reality an *anhydrous bismuthic carbonate*, for which the author proposes the name "Bismuthospherite." All the natural carbonates of bismuth hitherto analysed were hydrated. C. A. B.

A peculiar Twin-formation of Cobalt-speiss. By G. VOM RATH (*Jahrb. f. Min.*, 1877, 405–406).—Naumann described a crystal-group of cobalt-speiss from the Daniel mine near Schneeberg, the crystals occurring in peculiar penetration-twins, the twin-axis being given by him as the normal to a face of $30\frac{3}{2}$, the individuals being developed prismatically parallel to the trigonal twin-axis common to both. Vom Rath examined some specimens of arborescent cobalt-speiss which undoubtedly exhibited the peculiar twin-formation described by Naumann, presenting a striking example of crystalline development in the direction of the trigonal axis. The twin crystals in question occur in a central rod-like aggregation, with three twisting arms projecting upwards from it at angles of 70°·30′. The whole of this peculiar tree-like structure is built up of the above-mentioned twins, all having an identical position, whence it follows that the structure represents a *single twin.* Whilst most of these crystals appear to correspond completely with those described by Naumann, as the re-entering angles intersect one another in the terminals of the crystals, there are other isolated crystals which exhibit a normal twin-formation, according to the law "the twin axis a triagonal axis." The twins, according to the last-mentioned law, completely resemble the well-known twins of fluorspar, galena, &c., and occur as penetration-twins, with a rotation of 60° and 180°, the combination observed being $\infty O\infty.O.\infty O.202$; all these faces being evenly and well-developed, most particularly the cubical faces, which are square. The author points out that the occurrence of these well-developed twin-crystals (which appear to be more inclined to isolation than to enter into the peculiar arborescent growth which was observed with the other penetration-twins), strongly shows that the twin-law of Naumann is not correct. The faces of the abnormal twins are always convex, particularly the cubical faces, as the terminal edges of these penetration-twins are not normal cubical edges, the interfacial angles never measuring 90°, but generally 100° to 105°. It was observed throughout that the Naumann twins never exhibited well-developed terminal edges, but mostly distortions of the occurring faces. Vom Rath concludes by stating that the twins described by Naumann are abnormal, the crystals appearing to penetrate each other in a different position, owing to the facial distortion, whilst those crystals which possess well-defined cubical faces occur in normal twins according to the law already given above. The distorted twins exhibit an acute rhombohedron at their poles instead of a cube. C. A. B.

Glauberite and Blödite of Pendshab. By W. SCHIMPER (*Jahrb. f. Min.*, 1877, 408).—*Glauberite* occurs attached to cubes of rock-salt, in forms having exactly the habit of the crystals from Westeregeln, near Magdeburg, which was described by von Zepharovich (*Jahrb. f. Min.*, 1874, 543). The forms observed were $0P.-P$, predominating; then $\infty P.\infty\bar{P}\infty$, with small developed faces, and sometimes also $-\frac{1}{2}P.2\breve{P}\infty.\frac{2}{3}\breve{P}\infty$ occur, but only very secondary.

Blödite.—These crystals fully exhibit the development described by vom Rath, Groth, and Hintze (*Jahrb. f. Min.*, 1872, 528) of the Stassfurt and Magdeburg blödite. The forms observed were—

$$0P.\breve{P}_{\infty}.-P.\infty P.\infty\bar{P}2,$$

being secondary, $\infty\breve{P}3.$ and $+\breve{P}4.$ C. A. B.

The Schorlomite of the Kaiserstuhl. By A. KNOP (*Jahrb. f. Min.*, 1877, 408—409).—The author came to the following conclusions after his examinations of this mineral:—1. Most analyses of titaniferous silicates, particularly of the melanite of the Kaiserstuhl and of Frascati, did not lead to satisfactory results, owing to the methods for the separation of this acid being imperfect. 2. The minerals from the Kaiserstuhl, which were always considered to be schorlomite, are either melanite or pyroxene (augite). Schorlomite *does not* occur at the Kaiserstuhl. 3. As the real American schorlomite occurs intergrown with melanite (both minerals possessing the same outward appearance and the same crystalline form, viz., $\infty O.2O2$), an accurate examination of the specimens is advisable, in order to ascertain whether the above-mentioned crystalline form is not peculiar to melanite, schorlomite being in that case amorphous. C. A. B.

Some Brazilian Minerals. By A. GORCEIX (*Jahrb. f. Min.*, 1877, 409—410).—*Euclase* is found accompanied by *topaz* in the neighbourhood of aluminous slates, embedded in a white clay or quartz, near Ouro Preto, 1½ miles from the quarries. The beautiful *colourless andalusites* and *green tourmalines* (called by the natives emeralds), are found in the north of the province Minas Novas, on the banks of the river Doce. *Black tourmalines* are common everywhere. Between Ouro Preto and Sabara, near the village Rio-das Pedras, there is a vein of granular quartz, quite filled with large crystals of black tourmaline. This variety of tourmaline is also found in the gold mines of Antonio Pereira, at the extremities of the veins. C. A. B.

Hydrocastorite, a New Mineral. By G. GRATTAROLA (*Jahrb. f. Min.*, 1867, 411).—Occurs as a mealy deposit upon kernels of castor, having the appearance of an aggregate of fine needles under the microscope. H., 2, spec. grav., 2·16. Colour, white. Double refractive in polarised light. Chemical composition as follows, viz.:—

SiO_2.	Al_2O_3.	CaO.	H_2O.
59·59	21·35	4·38	14·66 = 99·98

Hydrocastorite (which is undoubtedly a product of the decomposition of castor) is found in company with black and red tourmaline, beryl, castor and pollux, in veins of granite at San Piero, Elba.

Andalusite and Pinite from Elba.—Andalusite is found in felspar, at San Piero, in Campo. Forms observed . $\infty P.\infty \breve{P}2.0P$, also as radiating aggregates of crystals. The greenish crystals often envelop a dark-red kernel. Spec. grav., 3·244. Chemical composition as follows, viz.:—

SiO_2.	Al_2O_3 and Fe_2O_3.	H_2O.
39·16	58·53	1·58 = 99·27

The green incrustation enveloping the andalusite (which is a product of the decomposition of the latter), is *pinite*. Hardness, 2·5. Spec. grav., 2·75—2·86. Chemical composition as follows:—

SiO_2.	Al_2O_3.	Fe_2O.	K_2O.	Na_2O.	H_2O.
49·40	18·80	16·41	6·63	2·17	6·87 = 100·28

C. A. B.

Olivine Rock. By H. MÖHL (*Jahrb. f. Min.*, 1877, 413—414).—The rocks in which olivine is the predominating constituent are the dunite of New Zealand, and the lherzolite of the Pyrenees. Both are light green, and contain only a trifling amount of enstatite, diallogite, chromdiopside, and chrompicotite. The olivine-rocks of the Ulthenthal, and the bombs and blocks enclosed in basalt, contain a considerable amount of the above-mentioned minerals. The rocks of Sweden and Norway are particularly fine, and are only partially composed of olivine, but eulysite (a rock closely related to olivine rock) consists of olivine, diallagite, garnet, and magnetite. The eruptive olivine rocks of the Fichtelgebirge, Ellgoth in Austrian Silesia, and the Hessian Hinterland, between Dillenburg and Brilon, are very dark, blackish-green in colour, and were first accurately described by Gümbol and Sandberger. In the Hessian district they occur in mounds or points, ridges, and veins, the general strike being that of the transition-rocks. The author examined 45 points of eruption, and found that in most of them the olivine was more or less converted into serpentine (the Dillenberg specimen consisted almost entirely of serpentine), and associated with it were diallagite, magnesium-mica, chromdiopside, magnetite, chrompicotite, titanite, &c. Orthoclase and oligoclase occur in many localities, sometimes constituting about one-third of the rock, and passing over into gabbro. At Endbach the asymmetrical felspar is more prominent, and associated with granular olivine, which is completely converted into serpentine, whilst there is a diminished amount of the other rock-minerals already mentioned. Again at Rachelshausen and Oberdieten, the olivine rock is very closely allied to proterobase, in which the olivine has almost entirely disappeared, whilst oligoclase, augite, hornblende, chloropite, magnetite, titanite, and occasionally mica, constitute a granitic mixture, which shows that olivine rock may belong equally to the gabbro and the diabase series of rocks.

C. A. B.

The Limestones and Calcium Phosphates of Curaçao. By A. STELZNER (*Jahrb. f. Min.*, 1877, 415—416).—The calcium phosphates occur partially in the form of loose lumps resting upon the limestone, and partially in such a form as to show that they are a product of the decomposition of the limestone itself. The limestone is sometimes massive and sometimes oolitic, and penetrated by the remains of gasteropods and bivalves, from which it may be inferred that it is a very recent formation; a qualitative examination proved it to be passing gradually into calcium phosphate, the mass at the same time becoming cellular in structure. The purest calcium phosphate is found in nests or veins disseminated throughout the limestone; or it occurs in foliated shell-like masses, having a reniform surface, clothing, and even entirely filling the cells or hollows in the cellular limestone. In its pure state this calcium phosphate is an amorphous, yellowish, greenish, or brown mass, with a dull or resinous lustre upon its conchoïdal fractured surfaces, somewhat resembling opal in appearance. From its appearance and properties, it is undoubtedly the same substance as the pyroclasite of Shepard, the sombrerite of Phipson, and the hard guano of Dana. Formerly pyroclasite was supposed to be the result of volcanic action upon the coral-limestone, but it is known at present to have been formed by the action of water upon guano, the solution thus obtained acting upon the limestone, and causing the formation of calcium phosphates. An examination of the specimens of calcium phosphate from this locality seems to prove that the purest calcium phosphate was originally a gelatinous precipitate, which subsequently hardened, as bubble-like spaces are found in the shell-like masses, which could only have been formed by the generation of gas inside a permeable, gelatinous mass. This theory of the formation of natural phosphates agrees well with the chemical reaction between a solution of calcium phosphate and ammonia. Pyroclasite and the other phosphates above mentioned are therefore only hardened jellies. The occurrence of radio-fibrous crystalline calcium phosphates is very rare in Curaçao; they are probably the same as the mineral staffelite. Curaçao is an island belonging to the Antilles. C. A. B.

Note on an Edible Clay from New Zealand. By M. M. P. MUIR (*Chem. News*, xxxvi, 202).—The clay is from Mackenzie County, South Island. It is free from diatomaceæ. It is largely eaten by sheep.

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	NaCl(trace of KCl).	H_2O.	Organic.
61·25	17·97	5·72	1·91	0·87	3·69	7·31	1·77 = 100·49

M. M. P. M.

Meteorites. By J. LAWRENCE SMITH (*Compt. rend.*, lxxxv, 678).—A meteorite which, on the 21st December, 1876, passed over several of the States, projected fragments, one of which was found near Rochester, Indiana. It weighed 400 grams, and exhibited a globular texture. Spherical grains of two or three mm. diameter could easily be detached from the mass, with which they were identical in composition. Two silicates could be distinguished, but nothing resembling anorthite.

A meteorite fell at Warrenton, Missouri, on the 3rd January, 1877, of which the mineralogical composition was: peridote, 76·00; bronzite and pyroxene, 18·00; nickeliferous iron, 2·00; troïlite, 3·50; chrome iron, 0·50 per cent. This meteorite is unlike any yet described, except that of Ornans; it is very friable, and its crust is dull, and in parts scoriaceous.

A meteorite which fell at Cynthiana, Kentucky, on the 23rd January, 1877, weighed six kilos., and presented a great similarity to the meteorite of Parnallee. Its composition corresponded with peridote, 50·00; bronzite and pyroxene, 38·00; nickeliferous iron, 6·00; troïlite, 5·50; chrome iron, 0·52 per cent. R. R.

Organic Chemistry.

On Isodibutylene. By A BUTLEROW (*Liebig's Annalen*, clxxxix, 44—83).—Observing the extraordinary ease with which isobutylene becomes polymerised, the author was induced to undertake, in conjunction with Goriaïnow (*Liebig's Annalen*, clxix, 146), the study of the condensation products of the simpler members of the hydrocarbon series, C_nH_{2n}. In all cases in which the attempt has been made to obtain *methylène*, CH_2, condensation takes place, and *ethylene* is the result (Perrot, *Ann. Chim. Phys.* [3] xlix, 94; Butlerow, *Bull. Soc. Chim.*, 1862, xiii; and others). *Ethylene*, on the other hand, seems incapable of becoming polymerised, the source of the more complex bodies obtained when sulphuric acid acts upon alcohol being probably the higher alcohols contained in the latter. *Propylene*, although condensable by boron fluoride, gives neither di- nor tri-propylene, but only products of a higher order; nor do these bodies result from the action of sulphuric acid on normal or secondary propyl alcohol, Berthelot's experiments on this point (*Bull. Soc. Chim.* [2], xi [1869], 13) not being decisive. The author has also found that simple condensation-products cannot be obtained from isobutyl or from secondary butyl alcohol, although by abstracting water from the former, a hydrocarbon is obtained identical with the easily condensable isobutylene from trimethyl carbinol.

The action of sulphuric acid upon *isobutylene* itself led to no satisfactory result, since concentrated acid converts it at once into high-boiling products, and a weaker acid dissolves it, giving only a small quantity of condensed products, the most volatile of which is probably *isotributylene*, $C_{12}H_{24}$. When strong sulphuric acid acts upon trimethylcarbinol, the isobutylene first formed is also polymerised to high-boiling liquids. The quantity of these, however, decreases as more dilute acid solutions are employed, and when trimethyl carbinol is heated with twice its volume of a mixture of equal parts of sulphuric acid and water, only *isodibutylene* and unchanged *isobutylene* are obtained. The same result may be attained by enclosing isobutylene (liquified by cold) in a tube with dilute sulphuric acid, and after some days, when the hydrocarbon has dissolved, heating the tube in a water-bath. The condensed products separate on the surface of the acid; when dried (finally by boiling with sodium) they are fractioned. That portion which boils between 102—104° consists of *isodibutylene*, a colourless liquid, of sp. gr. at 0° = ·734.

Isodibutylene combines directly with bromine to form a rather unstable bromide, $C_8H_{16}Br_2$. By boiling with caustic potash, or even by distillation, this bromide is decomposed into HBr and $C_8H_{17}Br$. Fuming hydrochloric acid at 100° gives with isodibutylene a compound, $C_8H_{17}Cl$, which is a light oily body, stable at ordinary temperatures, but partially decomposed by distillation, HCl being given off. B.p. 145—150°.

An *iodide*, $C_8H_{17}I$, is obtained, with even greater ease, by saturating the hydrocarbon at 0° with hydriodic acid gas. This iodide is attacked, even at 0°, by moist silver oxide. The product of the reaction, dried by anhydrous baryta, consists of regenerated isodibutylene and a new octylic alcohol, $C_8H_{18}O$, named *isodibutol*. This alcohol is a colourless thick liquid of characteristic odour, which boils at 146·5—147·5°, and solidifies at 20°. Sp. gr. at 0° = ·8417. Its alcoholic nature is proved by its yielding, when treated with phosphorus pentachloride, the same chloride that is produced by the action of hydrochloric acid upon isodibutylene. It belongs to the class of tertiary alcohols, the general properties of which it shares. Its iodide, when treated with silver nitrite, gives neither a nitrolic nor a pseudonitrolic acid (Victor Meyer's test).

In order to determine its constitution, isodibutol was submitted to the regulated action of oxidizing agents; it gave, besides unaltered alcohol and isobutylene, the same products as are furnished by oxidation of isodibutylene, but no ketone or aldehyde, a further proof that it is neither a primary nor a secondary alcohol. It was only necessary then to study the oxidation of isodibutylene. This body was therefore treated in the cold for six days with a mixture of sulphuric acid and potassic dichromate. Carbonic acid was continuously evolved. The mixture was then distilled, that part of the distillate which contained oily drops being collected separately from the clear acid liquid which subsequently passed over. This clear liquid contained principally *acetic acid.* The first distillate was treated with potassic carbonate, when much of the oil dissolved. The undissolved oil was removed, and the remaining alkaline liquid again distilled. From the first portions of liquid which now passed over *acetone* was easily separated by potassic carbonate in excess; not, however, in large quantity, probably because much of it had been oxidized to acetic acid. The alkaline solution, after removal of the acetone and oil, gave, on treatment with sulphuric acid, acetic and *trimethyl-acetic* acids, of which several characteristic salts were prepared. Since trimethyl-acetic acid does not give acetone on oxidation, it is thus evident that the primary oxidation-products of isobutylene are *acetone* and trimethyl-acetic acid, thus: $C_8H_{16} + O_3 = C_5H_{10}O_2 + C_3H_6O$. The acetone is partially oxidized to acetic acid.

This experiment establishes the constitution of isodibutylene. For of the two products one contains *three*, the other two methyl groups; from which it must be inferred that the molecule of isodibutylene contains *five* such groups. Three of these must be united to one carbon-atom to form tertiary butyl $(CH_3)_3C—$, which appears in the trimethyl-acetic acid, the remaining two methyls forming with another carbon-atom the group $(CH_3)_2C=$, which by oxidation yields acetone. From these considerations the formula of isodibutylene may be inferred to be $(CH_3)_3C—CH=C(CH_3)_2$; and that of the corresponding tertiary alcohol isodibutol $(CH_3)_3C—CH_2—C(CH_3)_2OH$. The oxidation of the hydrocarbon follows the general rule for the series C_nH_{2n}, viz., that the carbon-atoms separate at the junction $C=C$.

$$(CH_3)_3C—CH=C(CH_3)_2 + O_3 = (CH_3)C—CO_2H + (CH_3)_2CO.$$

This constitution of isodibutylene granted, the mode of its formation from trimethyl-carbinol is the following: (1) part of the alcohol splits up into water and isobutylene; (2) one molecule of isobutylene unites with one of unaltered trimethylcarbinol, water being again eliminated. The course of the reaction is quite analogous to Collarits' and Merz's synthesis of aromatic ketones by the action of phosphoric anhydride upon a mixture of a hydrocarbon and an acid, or to Wischnegradsky's synthesis of diamylene (*Deut. Chem. Ges. Ber.*, viii, 434).

To account for the second phase of the reaction, the author remarks that methyl groups and their derivatives are in general less prone to enter into reaction than the groups $=CH_2$ or $\equiv CH$, and their derivatives. The different degrees of stability are well observed in the alcohols of the three categories and the bodies allied to them, the radicles of the primary alcohols being least inclined to part with the hydroxyl or other simple radicles united to them, while in the tertiary alcohols and their allies such separations take place with the greatest ease. When therefore trimethylcarbinol is partially resolved into water and isobutylene, the feebly-bound hydroxyl of the undecomposed alcohol combines more readily with the hydrogen in the group $=CH_2$ of the hydrocarbon than with that belonging to the more stable methyl-groups of its own molecule, thus—

$$(CH_3)_3C\boxed{(OH) + H}CH=C(CH_3)_2 = (CH_3)_3C—CH=C(CH_3)_2 + H_2O.$$

On the other hand, when isobutyl alcohol, $CH_2(OH)—CH(CH_3)_2$, separates partially into water and this same (iso-) butylene, no such condensation takes place, because the alcoholic hydroxyl unites with the hydrogen of the group $\equiv CH$ in its own molecule, rather than with that of the $=CH_2$ of isobutylene.

These considerations, somewhat modified, will also explain why secondary butyl alcohol, on treatment with sulphuric acid, gives, as a principal product, pseudo-butylene, but no dibutylene. Here the alcoholic hydroxyl tends to combine either with the hydrogen of the pseudo-butylene, $CH_3—CH=CH—CH_3$, first formed, or with that of the $=CH_2$ in its own molecule. The proximity of the latter determines its union with it, and consequently the complete conversion of the alcohol into pseudobutylene.

The higher-boiling portions of the oily acids from the oxidation of isodibutylene were, after a tedious investigation, found to consist of trimethylacetic acid and a new *octylic* acid, $C_8H_{16}O_2$, the separation of which was ultimately effected by preparing the cadmium salts, and fractionally distilling the acids extracted from them. This octylic acid is a colourless oily liquid, smelling like trimethylacetic acid, and boiling with partial decomposition at 205—218°. Its constitution is best expressed by the formula, $C(CH_3)_3—CH_2—CH(CH_3)COOH$: since the carboxyl group must be formed at the expense of one of the five methyl groups of isodibutylene, and it is reasonable to assume that the group oxidised is one of those lying nearest to the point of attack of the oxidizing agent, the doubly-united carbon atoms $C=C$. The formation of this acid from isodibutylene appears strange at first sight, but is not without analogy, since oxidation of the hydrocarbons C_nH_{2n}, appears in general to furnish the same products as that of the corresponding tertiary alcohols. Thus the author has found that a certain quantity of isobutyric acid may be obtained by oxidation of trimethylcarbinol. Now this octylic acid may be regarded as isobutyric acid in which hydrogen is displaced by tertiary butyl $(CH_3)_3C—$, isodibutol and isodibutylene being similarly derived from trimethylcarbinol and isobutylene respectively. It may be assumed that in both cases, by the successive removal and addition of water, an isomeric alcohol is first produced, which is then oxidized to the acid. Thus, when trimethyl carbinol is oxidized—

$$(1.)\ (CH_3)_3C(OH) = CH_2=C=(CH_3)_2 + H_2O.$$
$$(2.)\ CH_2=C=(CH_3)_2 + H_2O = (CH_3)_2CH—CH_2OH,$$

which furnishes isobutyric acid $(CH_3)_2CH—CO_2H$; and when isodibutylene is oxidized—

$$(1.)\ Bt—CH=C=(CH_3)_2 + H_2O = Bt—CH_2—C(OH)(CH_3)_2;$$
$$(2.)\ Bt—CH_2—C(OH)(CH_3)_2 = Bt—CH_2C(CH_3)=CH_2 + H_2O.$$
$$(3.)\ Bt—CH_2—C(CH_3)=CH_2 + H_2O = Bt—CH_2—C(CH_3)H—CH_2OH,$$

which yields the above octylic acid.

In support of this explanation the author mentions that he has found, amongst the oxidation-products of isodibutylene, a body derived from the octylene, $C(CH_3)_3—CH_2—C(CH_3) = CH_2$, whose existence is assumed in equations (2) and (3). This hydrocarbon would, upon oxidation, separate at the doubly-joined carbon atoms, and give, as a first product, a ketone, $C(CH_3)_3—CH_2—CO—CH_3$; and, in fact, the oily products insoluble in potassic carbonate were found to consist of a mixture of isodibutylene, and of a ketone of this composition boiling between 125 °and 130°. The peculiar deportment of this body with metallic sodium, which indeed first drew attention to it, is also exhibited by an undoubted ketone, namely, *ethylisopropyl ketone*, prepared by acting with zinc-ethyl on isobutyryl chloride; these bodies do not attack the metal in the cold, but dissolve it rapidly when warm, giving solutions which, in contact with air, quickly assume a blood-red colour, finally passing into brown. On the other hand, it is not oxidized by silver oxide; it does not combine with acid sodium sulphite, nor does it throw down ferric hydrate when boiled with ferric chloride, properties which distinguish it from the aldehydes and oxides of the class to which ethylene oxide belongs. Finally, when oxidised with sulphuric acid and potassic bichromate, it yields acetic and trimethylacetic acids, as follows :—

$$C(CH_3)_3—CH_2—CO—CH_3 + O_3 = C(CH_3)_3—COOH + CH_3(COOH).$$

This reaction is decisive with respect to its constitution.

The views unfolded in this paper receive some support from the author's observations on the action of sulphuric acid upon amylene (trimethylated ethylene) from tertiary amyl alcohol. Here the successive assimilation and separation of water take place without any change in position of the hydroxyl. In the cold sulphuric acid converts this amylene into diamylene. But when tertiary amyl alcohol is heated to 100° in a tube with three times its volume of a mixture of equal weights of sulphuric acid and water, the principal product is uncondensed amylene, which floats on the surface of the acid. If now the tube be laid on its side for some days, and occasionally shaken, the hydrocarbon again dissolves, *i.e.*, assimilates water to reproduce the alcohol; and these operations may be repeated several times. Here, then, is an example of dissociation, and of gradual union of the dissociated bodies to form the original compound. In the case of isodibutol, on the other hand, the dissociated products (isodibutylene and water) would reunite to form, not the original alcohol, but an isomeride.

Let it be supposed that, in a mixture of tertiary alcohol and sulphuric acid, some molecules are dissociated even at low temperatures, as Wislicenus has observed for concentrated lactic acid, and Berthelot for saline solutions. Under ordinary conditions chemical equilibrium is established when a small number of hydrocarbon molecules and a large number of molecules of alcohol are present; in the warm mixture, on the contrary, the hydrocarbon molecules preponderate. It may now be assumed, (1) that in certain cases the dissociated products unite to form, not the original molecules, but new ones isomeric with them; and (2) that these new molecules also undergo dissociation. Under these circumstances chemical equilibrium would be established between certain quantities of the two isomeric alcohols, the hydrocarbon and water. Such a condition of equilibrium might even occur in the absence of a reagent, such as sulphuric acid, to bring it about, and the composition of an apparently homogeneous mixture might then be different at each moment of time. Between the isomeric molecules present there would be the same "struggle" ("Concurrenz" Pfaundler, *Pogg. Annalen*, 1874, Jubelband, p. 189) which takes place between molecules of different kinds. In most homogeneous gaseous or liquid substances the number of molecules of one kind is exceedingly great, that of molecules of one or more other kinds, vanishingly small; the chemical *structure* of such a body may fairly be discussed. Cases however may occur, in which the quantity of one of the isomeric bodies present is not infinitesimal; here, then, the molecules of the two kinds would be in a state of continual "struggle." This, of course, renders the investigation of such a mixture difficult. since its reactions must vary with the conditions of experiment. As examples of such duality of structure, cyanic and hydrocyanic acids might be cited. From this point of view it is impossible, and indeed unnecessary, to determine whether cyanic acid is really carbimide or a hydrate of the radicle cyanogen, or whether hydrocyanic acid is a nitril or a carbylamine. By the adoption of such views our conceptions of chemical constitution would acquire a less absolute meaning; but many phenomena, as, for example, the frequent appearance of secondary products in reactions, would be explicable. Ch. B.

Constitution of Amylene from Fermentation Amyl Alcohol. By ELTEKOFF (*Deut. Chem. Ges. Ber.*, x, 1904—1905).—The author establishes the presence of the hydrocarbons

$$(CH_3)_2CH.C{\equiv}CH \text{ and } CH_3.CH_2.CH = CH.CH_3$$

in ordinary amylene. The latter he regards as being formed from the optically active alcohol, in virtue of a re-arrangement of its atoms, precisely as trimethylethylene is formed from the optically inactive alcohol. C. F. C.

Formation of Allylene from Bromocitrapyrotartaric Anhydride. By E. BOURGOIN (*Compt. rend.*, lxxxv, 710).—Bromocitrapyrotartaric anhydride was dissolved in water, saturated with ammonia, and to the solution excess of silver nitrate was added, then the mixture was heated for some hours at 130°, in sealed tubes. When the tubes were opened, a larger quantity of gas was disengaged, consisting of carbon dioxide and allylene, some of which gave the characteristic yellow precipitate with ammonio-cuprous chloride. The bromocitrapyrotartrate of silver appears to have split up, as shown by the equation:—$C_5H_4AgBrO_4 = AgBr + 2CO_2 + C_3H_4$. R. R.

Action of Sodium on Tetrachloromethane and Bromobenzene. By J. GUARESCHI (*Deut. Chem. Ges. Ber.*, x, 1748).—When sodium is added to mixed ethereal solutions of these substances, a violent reaction takes place, sodium chloride and bromide being deposited. Amongst the products are *pentaphenylethyl chloride*,

$$(C_6H_5)_3C—C(C_6H_5)_2Cl,$$

diphenyl, two other substances melting at 61·5° and 83°, and chlorinated compounds. J. R.

On the Limits of Etherification. By M. BERTHELOT (*Compt. rend.*, lxxxv, 883).—During the researches of the author and Saint-Gilles, on etherification, sixteen years ago, a certain number of mixtures were put aside in sealed tubes. The author now gives the results of the reactions.

Equivalent Weights of Ethyl Alcohol and Acetic Acid.—Two specimens prepared in 1862, contained, in November, 1877, 65 and 65·4 per cent. of acetic ether respectively. These numbers approach very near to those obtained in the original experiments (*Ann. Chim. Phys.* [3], lxviii, 239), by heating the mixtures in sealed tubes nearly full of liquid.

In presence of water the same results are obtained; a mixture of acetic acid and alcohol with 4 per cent. of water contained, after 8 years, 63·8 per cent. of acetic ether, coinciding with the limit obtained in the original experiments (*loc. cit.*, p. 301).

Another experiment, with equivalent weights of glycerin and acetic acid, gave, after 6½ years, 71 per cent. of etherified acid. The limit obtained by heating the mixtures was 69·3.

Tartaric Acid and Alcohol.—A mixture of 28 per cent. alcohol, 11·8 per cent. tartaric acid, and 60·2 per cent. water, left for 12 years, had lost 32·2 per cent. of its original acid. The same mixture when heated, had lost 32·5 per cent. This acid, being bibasic, existed partly as neutral ether, partly as ethyl-tartaric acid. The present mixture contained 1·3 per cent. of neutral ether, 5 per cent. of ethyltartaric acid, and 5·5 per cent. of unchanged acid. The mixture obtained by heating to 135°, contained 1 per cent. neutral ether, 5·7 per cent. ethyltartaric acid, and 5·1 per cent. of unchanged acid. A mixture of ordinary alcohol and valeric acid, left at the ordinary temperature for 16 years, contained ethyl-valeric acid and water, *which had separated in the liquid form at the bottom of the tube.* In this tube the percentage of etherified acid was 81·7, instead of 65·8 obtained at 200°. This difference is due to the fact, that at 200° the water does not separate, whilst at the ordinary temperature it is removed from the field of action, and thus allows the etherification to go on further.

These experiments verify the general laws of etherification, and particularly the identity of the limits of combination between alcohols and acids, from the ordinary temperature up to 260°. C. W. W.

Etherification of Secondary Alcohols. By N. MENSCHUTKIN (*Deut. Chem. Ges. Ber.*, x, 1898—1902).—The results of this investigation are contained in a comprehensive table, from which it is seen:—

(*a.*) That the absolute initial velocities of etherification of the secondary alcohols are about 30 less than those of the corresponding primary alcohols. They differ from one another, the velocity being greatest in the case of dimethyl carbinol; less by 3 in that of ethylmethyl carbinol, again decreasing by 3 in the case of methylisopropyl carbinol, but at this point remaining constant for all secondary alcohols containing four or more carbon-atoms.

(*b.*) Whereas the absolute velocities of etherification during the first hours of observation are practically the same for all primary alcohols, these observed velocities for the secondary alcohols are found to differ from one another, even in cases where the initial velocities are identical. Further, the absolute velocities observed during the second and subsequent hours are greater for the secondary than for the corresponding primary alcohols.

(*c.*) During the earlier hours, greater velocities are observed in the case of alcohols of smaller molecular weights; after the lapse of 36 hours these differences disappear, the etherification during this interval being found equal for all secondary alcohols hitherto investigated. Subsequently the velocities of etherification of the secondary alcohols increase with increase of molecular weight.

(*d.*) The relative initial velocities are found to decrease with increase of molecular weight, and are much smaller than those of the corresponding primary alcohols.

(*e.*) Of the secondary unsaturated alcohols, both absolute and relative initial velocities are less than those of the saturated alcohols.

(*f.*) The observed limit of etherification exhibits a percentage increase of 1·1 for each carbon-atom added to the alcohol molecule. The limit is less for the corresponding unsaturated alcohols.

The author finds that the etherification of methylisopropyl carbinol follows a somewhat abnormal course, which fact he refers to a conversion of the alcohol on prolonged heating into the isomeric dimethylethyl carbinol. Secondary octyl alcohol exhibits a similar deviation, which is similarly explained. C. F. C.

Action of Methyl Iodide upon Sulphur. By H. KLINGER (*Deut. Chem. Ges. Ber.*, x, 1880—1881).—By heating methyl iodide (2 mols.) with sulphur (1 mol.) in sealed tubes to 160—190°, the author has obtained trimethysulphiodide, crystallising from alcohol in colourless prisms. The corresponding free base is at ordinary temperatures a heavy oil, soluble in water in all proportions; its aqueous solution exhibits strongly alkaline properties, and does not undergo decomposition on boiling.

The author has obtained the platinochloride, $\{(CH_3)_3S.Cl\}PtCl_4$, crystallising in a form compounded of the cube and octahedron.

C. F. C.

Brominated Ethylic Ether. By FR. KESSEL (*Deut. Chem. Ges. Ber.*, x, 1667—1676).—The author has obtained, by the action of bromine on ethylidene oxychloride, $[(CH_3—CHCl)_2O + 16\ Br]$, in sealed tubes at 210°, the following amongst other products:—

1. $C_4H_2Br_8O$ (octobromether), a thickish liquid, fuming slightly in the air, insoluble in water. It is decomposed by distillation at ordinary pressure, but distils at 132—135° at reduced pressure (450—470 mm.).

2. $C_2H_2Br_4$, a body crystallising in pearly scales, easily soluble in ether, alcohol, and carbon bisulphide, insoluble in water. It melts at 52°, and boils at 220°.

3. Tribromacetic acid.

Bromine acting on ethylidene oxychloride $[(CH_3—CHCl)_2O + 4Br]$ in open vessels at 100° forms a syrupy, yellowish liquid, which fumes in the air, and is decomposed by distillation. Its composition agrees with the formula, $C_4H_6B_4O$ (tetrabromether). The same substance is formed by saturating ethylidene oxychloride with bromine, at 115—120°.

The foregoing brominated ethers (octobrom- and tetrabrom-ether) are both decomposed by heating with water, the former yielding hydrobromic acid and bromoform, the latter hydrobromic acid, crotonaldehyde, and resinous products. From the analogy of this behaviour with that of ethylidene chloride (which yields hydrochloric acid by decomposition with water), the author concludes that the brominated ethers both contain the residue, —CHBr—O—CHBr—, and accordingly assigns to them the following formulæ :—

$CBr_3—CHBr—O—CHBr—CBr_3$ (octobromether);
$CH_2Br—CHBr—O—CHBr—CH_2Br$ (tetrabromether).

J. R.

Action of Sulphuric Acid on Mixed Ethers. By ELTEKOFF (*Deut. Chem. Ges. Ber.*, x, 1902—1904).—The author has further investigated the decomposition of ethyl-isocrotyl oxide by sulphuric acid (1 per cent.), and has proved that this ether is formed in accordance with the equation—

$$(CH_3)_2.C=CH.OC_2H_5 + H_2O = (CH_3)_2.CH.COH + C_2H_5OH,$$

its formation being therefore analogous to the similar decomposition of the simple and mixed ethers. Ethylisopropyl oxide is entirely decomposed, on heating with the dilute acid, into ethyl and isopropyl alcohols; this property of ready decomposition the author regards as peculiar to all ethers of secondary and tertiary alcohols. Ethyl-allyl oxide subjected, as a type of unsaturated compounds, to the same action, was resolved into ethyl and allyl alcohols; this result disproves Butlerow's view of the decomposition of the ethers of unsaturated alcohols at the point of union of the carbon-atoms by the double bond. The author further shows that ready resolution of these bodies is conditioned by the presence of unsaturated radicles.

The formation of ethylene by the action of Na upon $CH_3.CHCl_2$, the author regards as occurring in two stages, the first consisting in the resolution of the latter body into $CH_2CHCl + HCl$; the second in the reduction of the vinyl chloride thus formed to ethylene.

C. F. C.

Selenium-compounds. By L. v. PIEVERLING (*Liebig's Annalen*, clxxxv, 331—339).—*Ethyl Monoselenide.*—The author obtains this substance by digesting phosphorus pentaselenide (P_2Se_5) with potassium ethysulphate, potash, and water at 50° and submitting the product to fractional distillation. The distillate consists for the most part of ethyl monoselenide, contaminated, however, with traces of diselenide, which are removed by digesting the distillate with more potassium ethylsulphate, potash, and water, with the addition of a little phosphorus, and distilling afresh.

Pure ethyl monoselenide, $(C_2H_5)_2Se$, thus obtained is a clear, colourless, mobile, highly refractive liquid, smelling like the light hydrocarbons and boiling at 108°. It mixes with alcohol and ether in all proportions.

Triethyl-selenonium Iodide.—Ethyl monoselenide and ethyl iodide, when mixed in molecular proportions, combine slowly at the ordinary temperatures to form white crystals of the compound $Se(C_2H_5)_3I$. This substance is stable in the air, not hygroscopic, but very easily soluble in water and alcohol, and sparingly in ether. It sublimes completely between 80° and 126° without melting, but undergoing dissociation into ethyl monoselenide and ethyl iodide, which collect in the receiver and recombine in the course of 12 hours to form triethyl-selenonium iodide. The author finds by direct experiment that triethyl-telluronium iodide behaves in the same manner.

Triethyl-selenonium Hydroxide, $Se(C_2H_5)_3HO$.—This substance is formed by the action of silver oxide on triethyl-selenonium iodide. It is a powerful base, forming a syrupy solution which absorbs carbon dioxide and water with avidity. Its salts are all crystalline: they have the odour of leeks and a burning bitter taste. With the exception of the tartrate, they all deliquesce rapidly in the air, and hence cannot well be analysed.

The *tartrate*, $Se(C_2H_5)_3C_4H_5O_6 + 2H_2O$, crystallises in delicate needles of a pale rose-red colour: it dissolves very easily in water, forming an acid solution.

The *platinochloride*, $[Se(C_2H_5)_3Cl]_2PtCl_4$, crystallises in highly refractive red rhombohedrons.

From the foregoing results the author arrives at the conclusion that selenium is an element of variable atomicity, being bivalent in the compound $(C_2H_5)_2Se$, and quadrivalent in the compounds—

$$(C_2H_5)_2SeC_2H_5I \text{ and } (C_2H_5)_2SeC_2H_5(OH).$$

J. R.

Action of Alcoholic Soda on Etheric Nitro-compounds. By Filipp Hess and Johann Schwab (*Wien. Akad. Ber.*, lxxv, 702).—Beckerheim has proposed to determine the amount of nitro-substitution in such substances as nitroglycerin, nitrocellulose, &c., by saponification with standard alcoholic potash and titration of the alkali not converted into nitrate. The authors find that this process gives results far too high, as the reaction is a complex one, nitrite being formed and the alcohol (and possibly the glycerin) being oxidised to acetic and formic acids, aldehyde-resin, &c. Thus a specimen of nitroglycerin gave 15·72 and 15·65 per cent. of nitrogen by Dumas's method (after correction by the results of a blank experiment with pure glycerin, whilst 25·3 and 26·0 were found by Beckerheim's process. Analogous results appear to be produced with nitrocellulose, nitromannite, and similar bodies. Probably Beckerheim's process would answer were the nitrite reduced to ammonia by nascent hydrogen and then estimated as such.

C. R. A. W.

Sugar in Grapes. By E. Mach (*Dingl. polyt. J.*, ccxxv, 470—474).—In investigating the formation of sugar in plants the author and F. Kurmann have examined numerous samples of must by means of Fehling's solution and the polarizing apparatus of Ventzke and Soleil.

Fifteen samples of grapes examined on October 1st, 1875, gave an average difference of 0·5 per cent. of sugar between the polarizing method, in which the sugar was calculated as inverted, and the method by Fehling's solution. On the 15th of October an average difference of 2·02 per cent. was obtained, and on November 3rd, 4 per cent. Grapes preserved in a cool place gave, on November 20th, 8 per cent. of difference, and on December 28th, a difference of 10·5 per cent. between the two methods. Hence the later the grapes are examined, the greater the error in calculating the sugar as inverted sugar, since the levulose seems to predominate more and more over the dextrose.

The juice of several samples of apples gave differences of from 1 to 13 per cent. The juice of pears gave from 5 to 20 per cent. difference. These show that the calculation as inverted sugar is erroneous.

Experiments made on fermenting must show that the levulose ferments most quickly at the first, but soon the dextrose is most rapidly acted upon.

Fresh must was set to ferment after the addition of about $1\frac{1}{4}$ per cent. of cane sugar. After four days 0·93 per cent. of cane sugar remained; after ten days 0·27 per cent.; after sixteen days the whole had disappeared, but the fermentation of the sugar originally present in the must was completed only after thirty-one days. From this and other experiments it is inferred that must treated with cane sugar will always yield wine giving a left-handed rotation, whilst must treated with commercial grape sugar will yield wine giving a right-handed rotation. J. T.

Physical Properties of Quercite. By L. PRUNIER (*Compt. rend.*, lxxxv, 808—810).—The specific gravity of quercite is 1·5845. It crystallises in the clinorhombic system, and the crystals have a dextrogyratory power, $[\alpha]_D = 24° 17'$. R. R.

Cyanogen-compounds of Gold. By C. G. LINDBAUM (*Deut. Chem. Ges. Ber.*, x, 1725).—The author has prepared and analysed the following compounds:—

Potassium Aurocyanide, KCy.CyAu.—Prepared by Himly's method.

Potassium Auricyanide, $KCy.AuCy_2 + 1\frac{1}{2}$ aq.—Formed by the action of potassium cyanide on perfectly neutral gold chloride.

Potassium Iodauricyanide, $KCy.CyAuI_2$ + aq.; *bromauricyanide*, $KCy.CyAuBr_2$ + 3 aq.; and *chlorauricyanide*, $KCy.CyAuCl_2$ + aq.; the last formed by the action of chlorine on the iodine-compound.

Sodium Aurocyanide, $NaCy_2Au$; *bromauricyanide*, $NaCy_2AuBr_2$ + 2 aq., formed by the direct action of bromine.

Ammonium Aurocyanide, $(NH_4)Cy_2Au$.—Gives off ammonium cyanide at 100°.

Barium Aurocyanide, $BaCy_2.Cy_2Au_2$ + 10 aq.; *iodauricyanide*, $BaCy_4Au_2I_4$ + 10 aq.; *bromaurocyanide*, $BaCy_4Au_2Br_4$ + 10 aq.; and *chlorauricyanide*, $BaCy_4Au_4Cl_4$ + 8 aq.

Strontium Aurocyanide, $SrCy_4Au_2$ + 3 aq., and the iodine, bromine, and chlorine-compounds crystallises with 10 aq., 7—10 aq., and 8 aq. respectively;

Calcium Aurocyanide, $CaCy_4Au_2$ with 3 aq., and the iodine- and bromine-compounds, with 10 aq.;

Cadmium aurocyanide, anhydrous, and *bromauricyanide*, $CdCy_4Au_2Br_4$ with 6 aq.

Zinc Aurocyanide, anhydrous, and brom- and chlor-auricyanides with 8 aq. and 7 aq.

Cobalt Aurocyanide; auricyanide, $CoCy_4Au_2Cy_4 + 9$ aq.; iod- and brom-auricyanides, with 10 aq. and 9 aq. J. R.

Dibrom-ethylcarbylamine. By M. TCHERNIAK (*Compt. rend.*, lxxxv, 711).—According to the author's analysis, dibrom-ethylcarbylamine has the formula $NC_3H_5Br_2$, and may be regarded as cyanate of ethyl, the oxygen of which has been replaced by bromine.

R. R.

Nitrosoguanidine. By M. JOUSSELIN (*Compt. rend.*, lxxxv, 548—550).—Nitrosoguanidine is obtained by dissolving nitrate of guanidine in excess of nitrous and fuming nitric acid. After the solution has stood for 24 hours, it is poured into an excess of cold water, when the nitrosoguanidine is precipitated in acicular crystals. These are colourless and flexible, soluble in hot water and boiling alcohol, insoluble in ether and chloroform. Submitted to a gradually increasing temperature, nitrosoguanidine loses ammonia at 220°, the crystals becoming opaque without change of form. At higher temperatures cyanogen compounds are given off and a stable yellow substance remains, which is probably hydromellone. R. R.

Action of Hydrogen Sulphide on Propyl Aldehyde. By W. ALEXEJEFF (*Deut. Chem. Ges. Ber.*, x, 1739).—By saturating with hydrogen sulphide an aqueous solution of propyl aldehyde acidified with hydrochloric acid, the author has obtained a colourless liquid, lighter than water, agreeing approximately in composition with the formula $C_3H_6O + C_2H_6S$. The further action of hydrogen sulphide results in the production of a viscid liquid, heavier than water, and having the characteristic odour of the thioaldehydes. This substance is still under examination. J. R.

Thialdehydes. By H. KLINGER (*Deut. Chem. Ges. Ber.*, x, 1877—1880).—By converting the amorphous or α-benzothialdehyde into the β-modification (m.p. 225°) by the action of iodine in small quantity on its concentrated solution in benzene, and heating the latter with metallic copper, the author obtains stilbene in the proportion of 60 per cent. of the weight of β-thiobenzaldehyde employed.

By the action of methyl iodide (26 grams) upon thiacetaldehyde (10 grams) the author obtains trimethyl sulphiodide, $(CH_3)_3SI$ (10 grams). This reaction corroborates the tri-molecular view of the constitution of thiacetaldehyde. It appears to take place according to the equation—

$$(CH)_3.S_3.(CH_3)_3 + 3CH_3I = S(CH_3)_3I. + (CH_3.CHI.S)_2.CH.CH_3.$$

The α-thiobenzaldehyde dissolves with difficulty in ethyl iodide, and is converted into the β-modification which separates in the form of fine needles. C. F. C.

Molecular Volumes of the Silver Salts of Organic Acids.

By H. SCRÖDER (*Deut. Chem. Ges. Ber.*, x, 1871—1875).—The author has continued his researches, and obtains results which further establish the existence of a simple numerical ratio between the molecular volumes of the silver salts of organic acids, that they are in fact multiples of a unit denominated by the author a "silberstere" = 5·14 = one-half the at. vol. of silver. In the case of the fatty acids the molecular increment of CH_2 determines an increase of 3 steres = 15·4 in the molecular volume of the corresponding silver salts. The author, however, finds that the molecular volume of normal silver caproate is less by 2 × 5·1 than that of its isomeride the salt of the fermentation acid, and that the mean of the two quantities thus differing, and not either of the quantities themselves, is identical with the number obtained by calculation from the observed mol. vol. of silver acetate. On the other hand, silver isovalerate exhibits in its mol. vol. the normal difference of 3 × 5·14, from the mol. vol. of the normal butyrate. The author further finds the mol. vol. of silver benzoate (cryst.) to be 20 × 5·14, and that of the succinate (cryst.) to be 17 × 5·14.

C. F. C.

On Brominated and Chlorinated Ethyl Acetate.

By F. KESSEL (*Deut. Chem. Ges. Ber.*, x, 1994—2000).—*Dibromethyl acetate*, $CH_3—CO—O—CHBr—CH_2Br$, is obtained by the action of bromine on monochlorethyl acetate at 100—103°. The product is a yellow oily liquid fuming strongly in the air; it is insoluble in cold water, but decomposes slowly on long standing; in boiling water it dissolves completely with decomposition, crotonic aldehyde being evolved. It distils with partial decomposition at 180—240°; under a pressure of 360 mm. it boils at 132°. The distillate thus obtained has the same refractive index as glass, and a sp. gr. of 1·962 at 17°.

Trichlorethyl acetate, $C_2H_3O_2.C_2Cl_3H_2$, is produced by acting on monochlorethyl acetate with chlorine in presence of a little iodine at 120°. It is an almost colourless syrupy liquid, and distils with partial decomposition at 250—280°. On boiling with water it yields acetic acid and other products. T. C.

Remarks on the Conversion of Chloral into Dichloracetic Acid.

By V. MEYER (*Deut. Chem. Ges. Ber.*, x, 1740).—With regard to Wallach's discovery of the conversion of chloral into dichloracetic acid, the author points out that it is a general property of aldehydes in alkaline solutions to take up the elements of water, one molecule of aldehyde being thereby reduced, while another is oxidised. Thus, benzaldehyde is converted into benzoic acid and benzyl alcohol—

$$2(C_6H_5—COH) + H_2O = C_6H_5—CH_2OH + C_6H_5—COOH.$$

Glyoxal is converted by alkalis into glycollic acid—

$$COH—COH + H_2O = CH_2OH—COOH.$$

Glyoxalic acid is resolved into glycollic and oxalic acids—

$$2(COOH—COH) + H_2O = CH_2OH—COOH + COOH—COOH.$$

In the analogous reaction with chloral, the hydrogen, instead of reducing a second molecule of the aldehyde, replaces an atom of chlorine, with simultaneous formation of hydrogen chloride—

$$CCl_3—COH + H_2O = CCl_2H—COOH + HCl.$$

The potassium cyanide in Wallach's reaction acts merely as a feeble base, facilitating the separation of hydrochloric acid, as is shown by the fact that silver oxide acts in the same manner (*Compt. rend.*, lxi, 953).

The analogy of the reactions of aldehydes and chloral is rendered more apparent by writing them thus:—

$$\begin{array}{ll} \text{I.} & C_6H_5—COH + H_2O = C_6H_5—COOH + H_2; \\ \text{II.} & C_6H_5—COH + H_2 = C_6H_5—CH_2OH. \end{array}$$

$$\begin{array}{ll} \text{I.} & CCl_3—COH + H_2O = CCl_3—COOH + H_2; \\ \text{II.} & CCl_3—COOH + H_2 = CCl_2H—COOH + HCl. \end{array}$$

J. R.

Action of Chlorine on Butyric Acid. By L. BALBIANO (*Deut. Chem. Ges. Ber.*, x, 1749).—Dry chlorine acts rapidly on warm butyric acid in direct sunshine, the products (with 2 mol. of chlorine to 1 mol. of the acid) being chiefly mono- and dichlorobutyric acids. These, when etherified by means of alcohol and hydrochloric acid, yield mainly *ethyl monochlorobutyrate*, the boiling point of which is 168—169° under 741 mm. pressure, and its sp. gr. 1·072 at 0°. The ether is decomposed by water, even in the cold, but more rapidly when heated, hydrochloric acid being formed. J. R.

Heptoic Acid (Œnanthylic Acid) from Œnanthol, and some of its Derivatives. By TH. MEHLIS (*Liebig's Annalen*, clxxxv, 358—372).—The author obtained œnanthylic acid by distilling œnanthol (from castor-oil) with twice its weight of a mixture of 1 vol. of strong nitric acid and 2 vols. of water. The product was purified by conversion into barium salt and fractional crystallisation, the pure œnanthylate crystallising first. Œnanthylic acid, liberated from the barium salt by sulphuric acid, is a clear, colourless, oily liquid of faintly aromatic odour and burning taste, nearly insoluble in water, but easily soluble in alcohol and ether. It boils at 219° (mercury entirely in vapour) without decomposition, and solidifies at −12° to a crystalline mass, which melts at about −5°. Sp. gr. = 0·916 at 21°. The following salts of the acid were prepared:—

Ammonium Salt.—Formed by adding ammonia to the acid. Easily soluble in water, alcohol, and ether. Not crystallisable.

Potassium Salt.—Obtained by neutralising an alcoholic solution of the acid with potassium carbonate. It is left on evaporation as a white silky mass, devoid of crystalline structure. The salt dried at 100° agreed in composition with the formula $C_7H_{13}O.OK$.

Barium Salt, $(C_7H_{13}O_2)_2Ba$.—Formed by boiling the acid with barium carbonate in excess. Crystallises from hot aqueous solution in white iridescent laminæ, melting at 238—239° with decomposition. Soluble in 64 parts of water at 22°, and moderately freely in boiling alcohol of 85 per cent.

Lead Salt, $(C_7H_{13}O_2)_2Pb$.—Formed by double decomposition of the ammonium salt and neutral lead acetate. Soluble in boiling water, from which it crystallises on cooling, in white silky laminæ melting at 78°.

Copper Salt.—Precipitated by the ammonium salt from cupric sulphate. A bluish-green powder, insoluble in water but soluble in boiling alcohol, which deposits it in blue-green prismatic crystals of the formula $(C_7H_{13}O_2)_2Cu$.

Silver Salt, $C_7H_{13}O_2Ag$.—A white bulky precipitate, turning brown in the light. Insoluble in cold water and alcohol, sparingly soluble in boiling water.

Ethyl Œnanthylate, $C_7H_{13}O.OC_2H_5$.—Formed by heating the silver salt with ethyl iodide. A clear, colourless, highly refractive liquid, insoluble in water but soluble in ether and alcohol, having a fruity odour and a burning taste. It distils at 186—188° without decomposition, and remains fluid at $-14°$. Sp. gr. = 0·871 at 21°.

Œnanthonitril, $C_7H_{13}N$.—This substance is formed, together with œnanthamide, by heating œnanthylic acid with potassium thiocyanate (Letts's reaction). It is a clear, colourless, neutral liquid, insoluble in water but soluble in alcohol and ether. It boils at 175—178°. Sp. gr. = 0·895 at 22°. The nitril is decomposed by boiling with potash, the products being potassium œnanthylate and ammonia. It speedily undergoes alteration in the air.

Œnanthamide, $C_7H_{15}NO$.—Formed together with the preceding compound. When pure, it is easily soluble in water, alcohol, and ether. It crystallises from water in iridescent laminæ and from alcohol in pointed needles. The melting point is 94—95° By boiling with water or with alkalis it is resolved into œnanthylic acid and ammonia.

The formation of the two preceding compounds is represented theoretically by the following equations:—

$$CNHS + C_7H_{14}O_2 = C_7H_{13}N + CO_2 + H_2S;$$
$$CNHS + C_7H_{14}O_2 = C_7H_{15}NO + CSO;$$

but in practice other decompositions go on at the same time, which very much reduce the yield of the above products.

Œnanthylic anhydride, $(C_7H_{13}O)_2O$, obtained by distilling the acid with phosphorus pentachloride and heating the resulting œnanthylic chloride with potassium œnanthylate, is a colourless, thick liquid having a neutral reaction, and boiling at 268—271° without decomposition. Sp. gr. = 0·932 at 21°. It reacts with ammonia to form an amide identical in every respect with that described above. J. R.

α-Methyl-β-oxybutyric Acid and α-Methylcrotonic Acid. By H. Rohrbeck (*Liebig's Annalen*, clxxxviii, 229—239).—It has been shown (*Annalen*, cxlix, 205) by Wislicenus that the ethylic ether of aceto-acetic acid is converted by treatment with sodium amalgam and water into the sodium salt of β-oxybutyric acid, and that the latter on heating splits up into water and solid crotonic acid (*Zeitschr. f. Chem.*, 1869, p. 325). The author finds that the same changes take place with the ethylic ether of aceto-methyl-acetic acid. This body also combines with nascent hydrogen and yields α-methyl-β-oxybutyric acid—

$$\begin{gathered}CH_3—CO—CH(CH_3)—CO.O.C_2H_5 + Na_2 + 2H_2O = \\ CH_3—CH(OH)—CH(CH_3)—CO.ONa + NaOH + HO.C_2H_5.\end{gathered}$$

The latter splits up on heating into water and α-methyl-crotonic acid, identical with that obtained by Frankland and Duppa from ethomethoxalic acid (*Annalen*, cxxxvi, 1). G. T. A.

α-Ethyl-β-oxybutyric Acid and Ethyl-crotonic Acid. By E. Waldschmidt (*Liebig's Annalen*, clxxxviii, 240—248).—The action of nascent hydrogen on the ethylic ether of aceto-ethyl-acetic acid gives rise to the formation of α-ethyl-β-oxybutyric acid, and this, on heating, is converted into ethyl-crotonic acid identical with that obtained by Frankland and Duppa by the action of phosphorous chloride on the ether of diethoxalic acid. G. T. A.

Action of Chloranhydrides and Anhydrides upon Bibasic Diatomic Acids. By R. Anschütz (*Deut. Chem. Ges. Ber.*, x, 1881—1887).—The decomposition of anhydrous oxalic acid by benzoyl chloride in excess is proved by the author to take place according to the equation:—$R''\begin{matrix}COOH\\COOH\end{matrix} + \begin{matrix}R'.COCl\\R'.COCl\end{matrix} = R''\begin{matrix}CO\\CO\end{matrix}O + \begin{matrix}R'CO\\R'CO\end{matrix}O + 2HCl.$ Benzoic anhydride in the proportion of 80 per cent. of the theoretical yield was obtained. (The author has determined the boiling point of the latter to be 360°, the thermometer being completely enveloped by vapour.) By heating succinyl chloride (1 mol.) with succinic acid (1 mol.), succinic anhydride was formed in quantity approaching the theoretical. From this result the author concludes that the formation of trichloracetic anhydride from trichloracetic acid and phosphorus trichloride is immediately referable to a similar decomposition of the trichloracetic acid by trichloracetyl chloride, formed in the course of the reactions, and the truth of this he has established by direct experiment. By the action of acetic anhydride upon the corresponding acids, the author has prepared the following anhydride:—*Diphenic* (m. p. 211—212°); *succinic* (118°); *phthalic* (127°): *camphinic* (216—217°). The decomposition is represented by the general equation:—

$$R''\begin{matrix}COOH\\COOH\end{matrix} + \begin{matrix}R'CO\\R'CO\end{matrix}O = R''\begin{matrix}CO\\CO\end{matrix}O + R'.COOH.$$

The decomposition of dibromosuccinic acid by acetic anhydride resulted in the formation of monobromomaleic anhydride (m. p. 125°; b. p. 215°), most probably in the manner indicated by the equations—

(1) $C_4H_4Br_2O_4 + (C_2H_3O)_2O = C_4H_3BrO_4 + C_2H_3O.Br + C_2H_4O_2$; and
(2) $C_4H_3BrO_4 + (C_2H_3O)_2O = C_4HBrO_3 + 2C_2H_4O_2$.

By the action of fuming hydrobromic acid (4 mols.) upon monobromomaleic anhydride (1 mol.), the author obtains isobromomaleic acid, together with varying quantities of the two dibromosuccinic acids. Having also observed the decomposition at high temperatures of isobromomaleic acid into water and monobromomaleic anhydride, the author draws the probable conclusion that isobromomaleic acid is monobromofumaric acid.

From a consideration of the results of this research the author proposes the inversion of the formulæ now assigned to maleic and fumaric acids on the one hand, and to the two dibromosuccinic acids on the other; but reserves the full discussion of the subject for a further communication. C. F. C.

Diethylic Acetosuccinate and its Derivatives. By MAX CONRAD (*Liebig's Annalen*, clxxxviii, 217—226).—Ethylic acetosodacetate was treated with a sufficient quantity of ethylmonochloracetate to saturate the sodium with chlorine. The product obtained yielded a liquid on fractional distillation between 254° and 256°, which consisted of $C_{10}H_{16}O_5$, a formula which agrees with that of diethylacetosuccinate. This body consists of a colourless liquid, which can be distilled unchanged, and possesses a faint ethereal smell. It is insoluble in water, soluble in alcohol, ether, benzene, and bisulphide of carbon. It is not coloured by ferric chloride, and can exchange a hydrogen atom for sodium.

No other compound was formed in the above reaction, neither the ethylic ether of succinic acid, nor dehydracetic acid being able to be detected. Diethylacetosuccinate yields on saponification with strong alcoholic solution of potash acetic and succinic acids, and this is no doubt the way in which the succinic acid of Nöldecke (*Liebig's Annalen*, cxlvii, 224) was formed. When it is decomposed with barium hydrate, however, it yields a ketonic acid, $C_5H_8O_3$. This β-acetopropionic acid consists of large plates, which are very hygroscopic, and melt at 31°. It is easily soluble in water, &c., and decomposes the carbonates. It is probably identical with the levulinic acid of Grote and Tollens (*Annalen*, clxxv, 181).

The ethyl ether of β-acetopropionic acid was also obtained as a colourless liquid, heavier than water, possessing a fragrant smell, and boiling at 203° to 205°. G. T. A.

Synthesis of Pyrotartaric Acid from Ethyldiacetic Acid. By MAX CONRAD (*Liebig's Annalen*, clxxxviii, 226—228).—To a saturated warm solution of sodium in ethylic acetoacetate diluted with benzene, the quantity of the ethylic ether of α-bromopropionic acid corresponding with the sodium was added. The product of the reaction was the ethylic ether of β-methylacetosuccinate. This body is capable of taking up an atom of sodium. On saponification with concentrated caustic potash, it yields pyrotartaric acid and β-acetoisobutyric acid.

G. T. A.

Action of Sulphuric Acid on Malic Acid. By W. Weith (*Deut. Chem. Ges. Ber.*, x, 1744).—Malic acid is resolved by boiling with dilute sulphuric acid (boiling point, 135°) into carbon oxide, carbon dioxide, and aldehyde—

$$\mathrm{COOH{-}CHOH{-}CH_2{-}COOH = CO + CO_2 + CH_3{-}CH(OH)_2;}$$
$$\mathrm{CH_3{-}CH(OH)_2 = H_2O + CH_3{-}CHO.}$$

J. R.

Asparagin-derivatives. By J. Guareschi (*Deut. Chem. Ges. Ber.*, x, 1747).—On evaporating mixed aqueous solutions of asparagin and potassium cyanate, there remains a syrupy mass, which, when saturated with hydrochloric acid, deposits crystals of a body having the composition of *amidosuccinuric acid*—

$$\mathrm{CO.NH_2{-}CH_2{-}CH.NH_2{-}COOH + KCNO + HCl =}$$
$$\mathrm{CO.NH_2{-}CH_2{-}CH.NH.CO.NH_2{-}COOH + KCl.}$$

This product crystallises from water in hard, colourless prisms, sparingly soluble in water, and nearly insoluble in ether and alcohol. It melts at 137—138° with decomposition, a portion of it being converted into *amidomalylureide*, $\mathrm{CO.NH_2{-}CH_2{-}CH.NH.CO.NH{=}CO}$, a body previously obtained by the author by fusing asparagin with carbamide. The acid corresponding with this amide,

$$\mathrm{COOH{-}CH_2{-}CH.NH.CO.NH{=}CO,}$$

is produced on boiling amidosuccinuric acid with hydrochloric acid.

J. R.

Production of Racemic Acid in the Manufacture of Tartaric Acid. By E. Jungfleisch (*Compt. rend.*, lxxxv, 805—808).—The author's observations and experiments lead him to explain the appearance of racemic acid in manufacturing operations on tartaric acid, by the united actions on the solutions of heat and alumina, or an analogous oxide. R. R.

The Distillation of Nitrobenzene, Ethylbromide, Ethylbenzoate, and Naphthalene by means of Steam. By A. Naumann (*Deut. Chem. Ges. Ber.*, x, 2014—2017).—This is a continuation of the author's previous paper on this subject (*Deut. Chem. Ges. Ber.*, x, 1421 and 1819; also p. 47 of this volume).

	Excess of temperature of vapour over that of the liquid.	B. P. of mixture.	Vol. of water which distils over with 100 c.c. of the substance.
Nitrobenzene	0·5°	99°	700 c.c.
Ethyl bromide ..	0·0	37	1·35 c.c.
Ethyl benzoate ..	0·4	99	581 c.c.
Naphthalene	1·4	99	548 c.c.

T. C.

Propyl-isopropylbenzene. By Paternò and Spica (*Deut.*

Chem. Ges. Ber., x, 1746).—This substance is formed by the action of cumyl chloride on zinc ethyl (*Deut. Chem. Ges. Ber.*, ix, 581). It boils at 211—213° (bar. at 754 mm.). Sp. gr. at 0° = 0·8713. By oxidation with diluted nitric acid it yields *propylbenzoic acid*, $C_3H_7.C_6H_4.CO_2H$, isomeric with cumic acid, and *homoterephthalic acid*, $CO_2H.C_6H_4.CH_2.CO_2H$. Propylbenzoic acid crystallises from ether and weak spirit in colourless needles, which dissolve also in benzene and chloroform, and melt at 138—139°. The crystalline *ammonium salt*, which is soluble in water, alcohol and ether, gives precipitates with salts of the heavy metals.

Homoterephthalic acid is nearly insoluble in all liquids. It is a yellowish powder, subliming at high temperatures, without melting. The silver and barium salts have been analysed. J. R.

Reactions of Bromocymene. By PATERNÒ and COLOMBO (*Deut. Chem. Ges. Ber.*, x, 1749).—A solution of bromocymene in xylene, mixed with a little ethyl acetate, is readily attacked by sodium-amalgam, the compound $Hg(C_{10}H_{13})_2$ being formed. This substance crystallises from alcohol in matted needles, which dissolve in benzene and xylene, melt at 134°, and sublime without decomposition.

Bromocymene, heated to 100° with a mixture of concentrated and fuming sulphuric acids, yields two crystalline sulpho-acids, which are difficult to separate. J. R.

Action of Sulphuretted Hydrogen on certain Nitro-compounds. By F. BEILSTEIN and A. KURBATOW (*Deut. Chem. Ges. Ber.*, x, 1992—1994).—When a current of sulphuretted hydrogen is passed through a warm alcoholic solution of dinitrochlorbenzene, $C_6H_3Cl(NO_2)(NO_2)$,[1 : 2 : 4], m. p. = 53°, to which a little strong ammonia has been added, *tetranitrophenyl sulphide* is precipitated as a yellow body. An alcoholic solution of potassium sulphide, or better, sulphhydrate may also be used. Tetranitrophenyl sulphide crystallises from glacial acetic acid in yellow prisms; it dissolves with great difficulty in glacial acetic acid, and is practically insoluble in benzene, alcohol, and carbon disulphide; it melts at 193°, and, when heated to 120° with fuming nitric acid, yields the *sulphione*, $[C_6H_3(NO_2)_2]_2SO_2$(?), which melts at 240° and crystallises in yellow prisms. The above results are not what might have been expected from those previously obtained by Willgerodt (*Deut. Chem. Ges. Ber.*, x, 1683), who found that dinitrophenyl mercaptan was produced by the action of aniline sulphydrate on the above dinitrochlorobenzene.

Nitroparadichlorbenzene, $C_6H_3.Cl.Cl.NO_2$[1 : 4 : 2], m. p. 55°, treated in a similar manner with ammonia, alcohol, and sulphuretted hydrogen or with potassium sulphydrate, gives *chloronitrophenylmercaptan*, $C_6H_3.(SH).Cl.NO_2$[1 : 4 : 2], crystallising in yellow plates, and melting at 212°; it is difficultly soluble in glacial acetic acid, still less so in alcohol and carbon disulphide, but more easily in benzene.

On treating the same nitroparadichlorobenzene with alcoholic potassium sulphide, *dichlorodinitrophenylsulphide* is produced, crystallising in yellow needles which melt at 149°. T. C.

Action of Aromatic Sulphonic Chlorides on Dimethylaniline. By W. MICHLER (*Deut. Chem. Ges. Ber.*, x, 1742).—The reaction of dimethylaniline with benzene-sulphonic chloride, benzene-disulphonic chloride, and naphthalene-sulphonic chloride, gives rise to beautiful blue colouring matters of extraordinary tinctorial power, together with colourless sulpho-compounds. The blue substances are basic and are decolorised by mineral acids.

Trichloromethyl-sulphonic chloride also reacts with dimethyl-aniline to form a colourless sulphuretted base. J. R.

Action of Potassium Nitrite on Nitraniline and Acetonitranilide. By ARMAND MÜLLER (*Chem. Centr.*, 1877, 204).—One equivalent of nitracetaniline or nitraniline, acidified with nitric acid, gives, on treatment with 1½ to 2 equivalents of potassium nitrite, and subsequently with strong ammonia, a deep red crystalline precipitate which dries up to a red-brown powder, while the mother-liquor contains diazoamidonitrobenzene. In its properties this substance corresponds with Vogel's "zinalin," prepared from a rosaniline salt with nitrous acid. It is sparingly soluble in water, but dissolves with red colour in alcohol, ether, chloroform, and carbon disulphide; it dissolves with deep blood-red colour in caustic alkalis, and is precipitated by acids in yellow flocks. It dyes silk a fine yellow. It is more easily prepared by dissolving 1 pt. of acetanilide in 8 pts. of nitric acid at 75°, adding an equal volume of boiling water, filtering through asbestos, and subsequent treatment with potassium nitrite and ammonia. It is probably phenol-di-diazonitrobenzene, $C_{18}H_{13}N_5O_3$. W. R.

Derivatives of Triamidobenzene. By H. SALKOWSKI (*Deut. Chem. Ges. Ber.*, x, 1692—1697).—Triamidobenzene, when boiled for some hours with twice its weight of glacial acetic acid, is converted into *acetylethenyl-triamidobenzene*, $C_6H_3(NH.C_2H_3O)(NH.C_2H_3)(NH_2) + 2H_2O$. This substance crystallises in prisms, which dissolve very freely in hot water, but scarcely at all in cold. It melts at 85—90°, and when carefully heated gives off its water at 100°. When treated with hydrochloric acid, it does not form the hydrochloride, but is resolved into acetic acid and *ethenyltriamidobenzene hydrochloride*. The latter substance forms brilliant reddish triclinic crystals, easily soluble in water. Its composition agrees with the formula $C_6H_3(NH_2)_2(NH.C_2H_3),2HCl + 1\frac{1}{2}H_2O$. J. R.

Orthonitro- and Orthamido-Benzonitril. By HÜBNER (*Deut. Chem. Ges. Ber.*, x, 1713).—Orthonitrobenzoyl chloride reacts with strong aqueous ammonia to form orthonitrobenzamide, which crystallises in long colourless needles melting at 174°. This substance, when heated to 180° with phosphorus pentoxide, yields orthonitrobenzonitril, $C_6H_4NO_2.CN$, a colourless crystalline body dissolving easily in water and alcohol, and melting at 109°.

Orthonitrobenzonitril, when treated with tin and hydrochloric acid, is converted into orthamidobenzonitril, $C_6H_4NH_2.CN$, which crystallises in yellowish needles, melting at 103°, and dissolving easily in water, alcohol, and ether. The same product is obtained by heating ammonium orthonitrobenzoate. J. R.

Action of Phosphorus Trichloride on Carbamides. By W. WEITH (*Deut. Chem. Ges. Ber.*, x, 1743).—Phosphorus trichloride acts violently on carbamide when heated with it over the water-bath. Ammonia is eliminated in the form of phosphamide-compounds, the other products being biuret and an amorphous substance, which from its composition appears to be triuret.

Monophenylcarbamide yields, by similar treatment, *monophenyl-biuret*, a crystalline substance sparingly soluble in water, but easily in alcohol and ether. The reaction is as follows:—

$$2(NH_2—CO—NHC_6H_5) = NH_2C_6H_5 + C_2O_2N_3H_4C_6H_5.$$

When monophenylbiuret is boiled with aniline, ammonia is expelled, and a fine crystalline substance, probably diphenylbiuret, is produced. J. R.

Action of α-Dinitrochlorobenzene on Thiocarbamide. By WILLGERODT (*Deut. Chem. Ges. Ber.*, x, 1686—1688).—α-Dinitrochlorobenzene dissolved in 90 per cent. alcohol reacts with thiocarbamide, when heated therewith in sealed tubes, in such a manner that the chlorine-atom of the benzene-compound is replaced by the group HS, the chief product of the reaction being *α-dinitrophenyl-mercaptan*, $HS.C_6H_3(NO_2)_2$. This substance crystallises in short yellow needles, which melt at 275—280°. Its formation may be represented by the equation:—

$$(NH_2)_2CS + C_2H_5OH + H_2O + C_6H_3(NO_2)_2Cl = C_6H_3(NO_2)_2SH + 2NH_3 + C_2H_5Cl + CO_2.$$

J. R.

Action of α-Dinitrochlorobenzene on Carbanilide. By WILLGERODT (*Deut. Chem. Ges. Ber.*, x, 1689—1691).—When these substances are heated to 200° with water in sealed tubes, the following reaction takes place:—

$$(NHC_6H_5)_2CO + C_6H_3(NO_2)_2Cl + H_2O = NH(C_6H_5)C_6H_3(NO_2)_2 + NH_2C_6H_5.HCl + CO_2,$$

the products being dinitrophenylaniline, aniline hydrochloride, and carbon dioxide in theoretical proportions. J. R.

Conversion of Nitrils into Imides. By A. PINNER and FR. KLEIN (*Deut. Chem. Ges. Ber.*, x, 1889—1897.)—When dry hydrochloric acid gas is passed into a mixture of benzonitril (1 mol.) and isobutyl alcohol (1 mol.), 2 mols. of the former are absorbed, and a crystalline body is obtained, which appears to be the chloride of a peculiar amide, having the formula $C_6H_5.C(Cl).OC_4H_9.NH_2.HCl$. This compound, if left over sodium hydrate, loses 1 mol. HCl, and is converted into a body whose constitution may be represented by the formula $C_6H_5.C(O.C_4H_9).(NH)''.HCl$. The latter salt is insoluble in ether, slightly soluble in benzene, and is freely dissolved by both alcohol and water; it is but very slowly decomposed by the latter. It is entirely decomposed at a temperature of 130—160° into benzamide and isobutyl chloride.

Compounds of this class are denominated by the authors *salts of benzamidoisobutyl ether.*

By the action of alcoholic ammonia upon this salt, a body is obtained crystallising in colourless silky needles, which is the chlorhydrate of benzimidamide, $C_7H_5.C.(NH)''.NH_2.HCl$; and in addition a thick oily liquid, the free base corresponding to the original salt, viz., benzimidobutyl ether, $C_6H_5.C.(NH)''.O.C_4H_9$. The authors have attempted, but without success, to prepare compounds of the form $R'.C(NH)''.OH$, isomeric with the amides, by passing HCl gas into the mixture of a nitril with the necessary quantity of water. C. F. C.

Reactions of Para-, Meta-, and Ortho-nitrobenzanilide. By H. Hübner (*Deut. Chem. Ges. Ber.*, x, 1708—1710).—1. *With Nitric Acid.*—The so-called paranitrobenzanilide (melting at 199°) is converted by the action of nitric acid into a *trinitrobenzanilide*, which melts at 165°, and may be resolved into metanitrobenzoic acid and dinitraniline melting at 176°. Hence its probable formula is—

$$CH_3.\overset{p}{N}O_2.\overset{o}{N}O_2.\overset{1}{N}H(\overset{1}{C}O.C_6H_4\overset{m}{N}O_2).$$

Orthonitrobenzanilide melting at 94° yields the same trinitrobenzanilide, thus confirming the correctness of the foregoing formula.

Metanitrobenzanilide melting at 154° gives with nitric acid three trinitrobenzanilides melting at 178°, 202°, and 212°. The first of these only has been fully examined. It may be resolved into a nitraniline melting at 175°, and orthonitrobenzoic acid.

2. *With Bromine.*—Paranitrobenzanilide, when treated with bromine, yields *orthobromoparanitrobenzanilide*, which crystallises in long colourless needles melting at 160°. This substance is resolved by potash into benzoic acid and orthobromoparanitraniline, which last is converted, by substitution of hydrogen for the amido-group, into nitrobromobenzene ($C_6H_4.NO_2.Br = 1:3$), crystallising in small yellowish prisms, and melting at 56°. The bromonitrobenzanilide yields by reduction orthobromoparamidobenzanilide, which crystallises in colourless laminæ, melting at 205°.

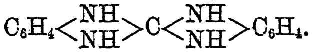
Together with orthobromoparanitrobenzanilide there is always formed a little paranitrodibromaniline melting at 203—204°.

Orthonitrobenzanilide, when treated with bromine, yields orthonitroparabromobenzanilide, which crystallises in fine yellow tablets, melting at 137°. The same compound is formed when parabromobenzanilide is treated with nitric acid. At the same time a dibromo-orthonitrobenzanilide, $C_6H_2Br_2(NO_2)NH.COC_6H_5$, is formed.

Dibromobenzanilide, obtained by the action of bromine on benzanilide, crystallises in colourless laminæ, and, when treated with fuming nitric acid, yields monobromodinitrobenzanilide, crystallising in colourless needles, and melting at 221°. The same compound is produced on treating orthonitromonobromobenzanilide with fuming nitric acid.

J. R.

Reactions of Amides with Cyanogen Iodide. By H. HÜBNER (*Deut. Chem. Ges. Ber.*, x, 1715—1720).—1. The author has shown previously (*Deut. Chem. Ges. Ber.*, ix, 776) that orthamidobenzene and cyanogen iodide react together to form a base having the formula $(C_6H_4.N_2H_2)_2C$. When this base, suspended in water, is treated with nitrous acid, an evolution of nitrogen dioxide takes place, and a red substance, $C_{13}H_8N_6O_3$, is precipitated, which dissolves readily in potash and ammonia, and forms with the latter a yellow crystalline compound. The formula assigned to the base is—



$$C_6H_4{<}\begin{matrix}NH\\NH\end{matrix}{>}C{<}\begin{matrix}NH\\NH\end{matrix}{>}C_6H_4.$$

2. Benzanilide, heated with cyanogen iodide, yields iodobenzanilide in reddish needles melting at 210°.

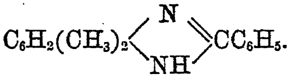
3. Paranitraniline, heated to 110—120° with cyanogen iodide, reacts in the following manner:—

$$4(C_6H_4NO_2.NH_2) + CNI = NH_4I + (C_6H_4NO_2.NH)_4C.$$

The latter product, which the author calls *carboparanitrotetramidobenzene*, forms small red crystals, melting above 300°. By reduction with tin and hydrochloric acid it yields the corresponding *amido-compound* $(C_6H_4NH_2.NH)_4C$, which crystallises in colourless tables, melting at 138°, dissolves easily in water, and volatilises without decomposition. The last substance reacts with nitrous acid to form a compound of the formula $(C_6H_4OH)_4.N_2O.(NO)_2C$.

4. Metanitraniline and cyanogen iodide yield *carbometanitrotetramidobenzene*, a green precipitate dissolving in aniline and alcoholic soda, and melting at 286°. It reacts in the same manner as the preceding para-compound. J. R.

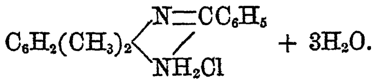
Anhydro-bases. By H. HÜBNER (*Deut. Chem. Ges. Ber.*, x, 1710—1713).—1. When xylidine obtained from coal-tar xylene boiling at 138—140° is treated with benzoyl chloride, the product is *α-benzoylxylidine* $C_6H_3(CH_3)_2.(NH.COC_6H_5)$, which crystallises from alcohol in colourless needles melting at 192°. On boiling this substance with strong nitric acid, a nitro-compound, $C_6H_2NO_2.(CH_3)_2(NH.COC_6H_5)$, is formed, which melts at 184·5°, crystallises from alcohol in yellow needles, and yields, by reduction with nascent hydrogen, α-anhydro-diamido-benzoylxylene—



$$C_6H_2(CH_3)_2{<}\begin{matrix}N\\NH\end{matrix}{>}CC_6H_5.$$

This substance crystallises from alcohol in colourless needles, melting at 195°. It forms crystallisable salts with hydrochloric, nitric, sulphuric, and oxalic acids.

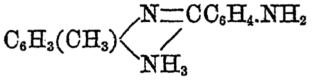
β-Xylidine, boiling at 198—210°, forms with benzoyl chloride *β-benzoylxylidine*, melting at 140°, and crystallising in colourless needles. The nitro-compound crystallises from alcohol in long needles melting at 178°; it yields by reduction an anhydro-compound, the hydrochloride of which crystallises in tables represented by the formula—



$$C_6H_2(CH_3)_2\left\langle\begin{matrix}N{=}CC_6H_5\\ /\\ NH_2Cl\end{matrix}\right. + 3H_2O.$$

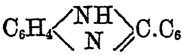
2. Benzomesidine, when subjected to the action of nitric acid, yields, together with trinitrobenzomesidine, a *mononitrobenzomesidine*, $C_6(CH_3)_3H.NO_2.NHCOC_6H_5$, the colourless crystals of which melt at 168·5°. From this compound nitromesidine, crystallising in golden-yellow needles, and melting at 75°, may be separated. The last-named substance reacts with metanitrobenzoyl chloride to form *metanitrobenzomesidine*, $C_9(CH_3)_3H_2.(NH.COC_6H_4.NO_2)$, which crystallises in colourless prisms, melts at 205°, and when treated with nitric acid yields *metanitrobenzodinitromesidine*, $C_6(CH_3)_3(NO_2)_2(NH.COC_6H_4.NO_2)$, (colourless needles, melting at 307°), and *metanitrobenzo-mononitromesidine*, $C_6(CH_3)_3.NO_2H(NH.COC_6H_4.NO_2)$, (colourless crystals, melting at 207°). The last substance is resolved by heat into nitromesidine and metanitrobenzoic acid.

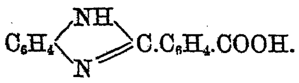
3. *Metanitrobenzo-paratoluide*, $C_6(CH_3)H_4.NH(COC_6H_4.NO_2)$, forms colourless needles, melting at 162°. With nitric acid it yields the compound $C_6(CH_3)H_3NO_2.(NHCOC_6H_4.NO_2)$, which crystallises in yellow needles melting at 188·5°. The last is readily converted into nitrotoluidine, $C_6H_3 : CH_3 : NO_2 : NH_2 (= 1 : 3 : 4)$, and metanitrobenzoic acid; it yields by reduction an anhydro-compound—



$$C_6H_3(CH_3)\left\langle\begin{matrix}N{=}CC_6H_4.NH_2\\ /\\ NH_3\end{matrix}\right.$$

which crystallises with 1 mol. of water in colourless laminæ melting at 228°.

4. *Anhydrotoluyldiamidobenzene*,  $C_6H_4\left\langle\begin{matrix}NH\\ N\end{matrix}\right\rangle C.C_6H_4.CH_3$, a colourless crystalline base melting at 268°, is formed, together with ditolyldiamide, by the reaction of orthamidobenzene and paratoluic chloride, or better by the action of orthonitraniline on paratoluic chloride. It yields by oxidation an *acid*, crystallising in long colourless needles, of the formula—

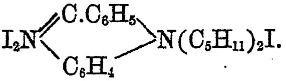


$$C_6H_4\left\langle\begin{matrix}NH\\ N\end{matrix}\right\rangle C.C_6H_4.COOH.$$

The analogous bases, *anhydrotoluyl-diamidotoluene* and *anhydrotoluyl-diamidoxylene* (melting point 217°) are obtained by similar reactions. They are both colourless crystalline bodies. J. R.

Action of Amyl Iodide on Anhydrobenzoyl-diamidobenzene.

By H. HÜBNER (*Deut. Chem. Ges. Ber.*, x, 1720—1722).—These substances react together to form a dark-red compound, which crystallises in very thin tables, soluble in alcohol and glacial acetic acid, and melting at 111—112°. The constitution of this body is represented by the formula—



$$I_2N\Big\langle\begin{matrix}C.C_6H_5\\C_6H_4\end{matrix}\Big\rangle N(C_5H_{11})_2I.$$

When its alcoholic solution is boiled with lead hydrate, it loses the whole of its iodine, and yields a base which crystallises from alcohol in laminæ melting at 90—91°. When recrystallised from water, however, the base melts at 164°.

An ethyl-compound analogous to the above is produced by substituting ethyl iodide for amyl iodide. It forms reddish-brown laminæ melting at 154—155°.
J. R.

Replacement of the Diazo-group by the Group SO_3H. By H. HÜBNER (*Deut. Chem. Ges. Ber.*, x, 1715). Dry metadiazoimidobenzoic acid, treated with alcoholic solution of sulphurous acid, yields metasulphobenzoic acid, $C_6H_4.COOH.SO_3H$. Similarly the paradiazo-compound yields parasulphobenzoic acid.
J. R.

New Mode of Formation of Phenetol. By AD. KASTROPP (*Deut. Chem. Ges. Ber.*, x. 1685)—The methods hitherto employed for the preparation of phenetol have involved the previous preparation of phenol-potassium and ethyl iodide. The author finds, however, that phenetol may be obtained directly in large quantity by heating a mixture of phenol and alcohol with zinc chloride, or by heating a solution of phosphorus pentoxide in phenol with alcohol.
J. R.

Compound of Sodium and Iron with a Derivative of Pyrogallol. By G. C. WITTSTEIN (*Chem. Centr.*, 1871, 621). By adding pyrogallic acid to a solution of an equal weight of ferric chloride, and then adding sodium carbonate, a nearly black precipitate is obtained containing soda and iron oxides, in the proportion of $2Na_2O + 2FeO + Fe_2O_3$, combined with an acid derived from pyrogallic acid.
M. M. P. M.

The Formula of Quinhydrone. By C. LIEBERMANN (*Deut. Chem. Ges. Ber.*, x, 2000—2002). In a paper by Wichelhaus (*Deut. Chem. Ges. Ber.*, x, 1781) the latter attempts to show that quinhydrone has the formula $C_{18}H_{14}O_6$, and that it is formed from one molecule of quinone and one of hydroquinone. The author contradicts these results, and points out that, assuming the formula $C_{18}H_{14}O_6$ as correct, quinhydrone must be formed from two molecules of quinone and one of hydroquinone; but this cannot be so, since the author has shown experimentally that it is formed from an equal number of molecules of quinone and hydroquinone, and that Wichelhaus' attempt to explain this latter fact by the equation $2C_6H_4O_2 + 2C_6H_6O_2 = C_{18}H_{14}O_6 + C_6H_6O_2$, is untenable. The author believes that the true formula is $C_{12}H_{10}O_4$, and that it is formed thus—$C_6H_4O_2 + C_6H_6O_2 = C_{12}H_{10}O_4$.
T. C.

On Quinhydrone. By R. NIETZKI (*Deut. Chem. Ges. Ber.*, x, 2003—2005).—By the action of sulphurous acid, quinone is converted easily and entirely into hydroquinone. In order, therefore, to ascertain the quantity of quinone present, it is only necessary to know the amount of sulphurous acid required, and this can be done by using a standard solution of the latter and titrating the excess with iodine, for the author finds that iodine has no action on the hydroquinone formed. This method is employed to settle the formula of quinhydrone, which, according to Wöhler and Liebermann, is represented by $C_{12}H_{10}O_4$, and according to Wichelhaus, by $C_{18}H_{14}O_6$; or for comparison these formulæ may be written respectively $C_{18}H_{15}O_6$ and $C_{18}H_{14}O_6$. Now since sulphurous acid reduces quinhydrone as well as quinone to hydroquinone, 4 atoms of hydrogen would be required according to the formula $C_{18}H_{14}O_6$, and only 3 according to $C_{18}H_{15}O_6$, to convert these bodies into hydroquinone $3(C_6H_6O_2)$. By titrating as above, it was found that only 3 atoms of hydrogen were required, and, therefore, that $C_{12}H_{10}O_4$ is the correct formula for quinhydrone.

A modification of the method (*Deut. Chem. Ges. Ber.*, x, 834) of obtaining hydroquinone from aniline is given, by means of which a much larger yield is got, 30 grams of aniline giving 10 grams of almost perfectly pure hydroquinone.

Investigations are being continued with regard to the action of solutions of toluquinone and hydroquinone on one another, and likewise of quinone on hydrotoluquinone. T. C.

The Formula of Quinhydrone. By H. WICHELHAUS (*Deut. Chem. Ges. Ber.*, x, 2005—2006).—This is a short reply to the two previous papers by Liebermann and Nietzki. The author believes "that phenoquinone, quinhydrone, and pyrogalloquinone are produced in such a manner that each molecule of quinone drives out two atoms of hydrogen from two molecules of phenol, hydroquinone, or pyrogallic acid, and then unites, by means of its own oxygen-atoms, with the affinities of the hydroxyl-oxygen-atoms thus set free." The hydrogen driven out as above is not liberated, but combines with the reducible substances (quinone and quinhydrone) present in the mixture. This is the answer to Liebermann's objections.

Wichelhaus thinks that the experiments of Nietzski are most fitted to settle the question, and intends to repeat them himself. T. C.

Derivatives of Rhenish Beech-wood Creasote. By W. BRÄUNINGER (*Liebig's Annalen*, clxxxv, 339—358).—The specimen of creasote examined by the author had the sp. gr. 1·04. It boiled between 180 and 216°, the greater part of the distillate passing over at 199—203°. It was found to contain traces only of phenol, and about 1·3 per cent. of cresol. By distillation over heated zinc-dust, it yielded anisol and a little toluene.

The portion of the distillate boiling at 199—203°, was violently attacked by melting potash, yielding pyrocatechin, but no traces of the oxybenzoic acids.

The creasote, when treated with potassium chlorate and hydrochloric acid, yielded *tetrachlorotoluquinone*, $C_6Cl_3.CH_2Cl.O_2$, a body previously obtained from beech-wood creasote by Gorup-Besanez, who described it as tetrachloroguaiacone. This substance is converted, by the action of sulphur dioxide into *tetrachlorotoluhydroquinone*, $C_6Cl_3.CH_2Cl.(HO)_2$, which sublimes in brilliant white brittle needles, soluble in alcohol and ether, and sparingly in water.

Tetrachlorotoluhydroquinone is converted by the action of dilute potash into *dichlorodioxytoluquinone-potassium*, $C_7H_2Cl_2(OK)_2O_2$, a red crystalline substance which is converted by dilute sulphuric acid into a brick-red crystalline powder, consisting of *dichlorodioxytoluquinone*, $C_7H_2Cl_2(OH)_2O_2$. J. R.

Nitracetophenone. By H. HÜBNER (*Deut. Chem. Ges. Ber.*, x, 1714).—Mononitro-acetophenone $(C_6H_4.NO_2)CO.CH_3$, is formed by the slow action of nitric acid on acetophenone at a low temperature. It is a colourless crystalline body, melting at 80—81°, and volatilising with steam. When treated with tin and hydrochloric acid, it is converted into *amidacetophenone*, the hydrochloride of which, $C_6H_4.NH_3Cl.CO.CH_3$, is a very deliquescent body.

Nitracetophenone is converted by oxidation into meta-nitrobenzoic acid. J. R.

Some Derivatives of Acetophenone. By H. HUNNIUS (*Deut. Chem. Ges. Ber.*, x, 2006—2011).—*Aceto-phenone bromide*, $C_6H_5.CO.CH_2Br$.—Emmerling and Engler, by the direct action of bromine on acetophenone, obtained the compound $C_6H_4Br.CO.CH_3$, which, on oxidation, gave monobromobenzoic acid (*Deut. Chem. Ges. Ber.*, iv, 148).—The author finds that on dropping 1 molecule of bromine into 1 molecule of acetophenone dissolved in carbon disulphide, a compound is produced, identical in percentage composition and similar in properties to the above, except that on oxidation it yields benzoic acid; nevertheless, for stated reasons, he thinks that the two are identical.

Acetophenone bromide is easily soluble in alcohol, ether, benzene, and chloroform; crystallises in colourless prisms, and melts at 50°.

Nitracetophenone bromide, $C_6H_4(NO_2).CO.CH_2Br$, is obtained by nitrating the above, in small needles, which melt at 96°, and dissolve in alcohol, chloroform, and carbon disulphide; they are very little soluble in ether and insoluble in water. On oxidation, it gives metanitrobenzoic acid.

Amidacetophenone, $C_6H_4.NH_2.CO.CH_3$, is obtained by reducing the last compound with zinc and hydrochloric acid, in the form of yellow crystals. The hydrochloride crystallises in colourless needles, which are very soluble in water.

Acetophenone acetate, benzoate, and alcohol were prepared, and agreed in all respects with those obtained by Hunäus and Zincke (*Deut. Chem. Ges. Ber.*, x, 1486).

Acetophenone dibromide, $C_6H_5.CO.CHBr_2$, is formed on treating acetophenone dissolved in carbon-disulphide with 2 molecules of bromine in the cold. It melts at 36° and is soluble in all ordinary solvents, except water. On boiling with caustic potash it yields benzoic acid, but with caustic soda an acid which appears to be benzoyl-formic

acid. By the action of alcohol and potassium acetate on the dibromide, the acetic ether is apparently produced, $C_6H_5.CO.CH(C_2H_3O)_2$.
T. C.

Dinitrobenzoic and Nitramidobenzoic Acids. By H. HÜBNER (*Deut. Chem. Ges. Ber.*, x, 1702—1704).—When dinitrobenzoic acid, obtained by the action of nitric acid on metanitrobenzoic acid, is converted into the nitramido-acid, and the NH_2-group in the latter is replaced by hydrogen, metanitrobenzoic acid is reproduced; and when the NH_2-group in nitramidobenzoic acid is replaced by chlorine, and the NO_2-group by hydrogen, metachlorobenzoic acid is formed. It follows, therefore, that both the NO_2-groups, and all the radicles replacing them, occupy the meta-position in relation to the carboxyl-group. Moreover, it becomes probable that *negative* groups or elements in general, in replacing hydrogen in benzoic acid, take the meta-position.

Dinitrobenzoic acid obtained as above, melts at 204—205°. Many of its salts and the ethyl-ether have been examined. By reduction with ammonium sulphide, it yields nitramidobenzoic acid, $C_6H_3.NO_2.NH_2COOH$. This substance melts at 208°, and crystallises from water in long golden-yellow needles. It yields by Griess's reaction metanitrobenzoic acid, and this, by further reduction, is converted into metamidobenzoic acid. Nitramidobenzoic acid likewise yields, through the diazo-compound, a chloronitrobenzoic acid, $C_6H_3.NO_2.Cl.COOH$, which crystallises in small, colourless, sparingly soluble needles melting at 147°. This body is converted by reduction with tin and hydrochloric acid into chloramidobenzoic acid, which crystallises from water in long colourless needles melting at 215—216°.

Metanitro-metamidobenzoic acid reacts with ethyl bromide to form nitro-ethylimido-benzoic acid, $C_6H_3NO_2.NHC_2H_5.COOH$, a body crystallising in small needles, dissolving sparingly in water, and melting at 208°. Its barium salt forms red needles.
J. R.

Di- and Tri-bromobenzoic and Dibromosalicylic Acids. By H. HÜBNER (*Deut. Chem. Ges. Ber.*, x, 1704—1708).—Metabromobenzoic acid, when acted on by nitric acid, yields α- and β-metabromo-orthonitro-benzoic acids. When the NO_2-groups in these latter are replaced by bromine (through the diazo-compounds) the following acids are formed:—

1. *α-Meta-ortho-bromobenzoic acid* (from α-metabromo-orthonitrobenzoic acid).—This substance crystallises in long needles, which dissolve sparingly in water and melt at 228°. Its *barium salt*, $(C_6H_3Br_2CO_2)_2Ba + 4\frac{1}{2}H_2O$, crystallises in colourless needles.

2. *β-Meta-ortho-bromobenzoic Acid* (from β-metabromo-orthonitrobenzoic acid) forms colourless needles melting at 153° and dissolving rather more freely than the α-acid. The *barium-salt* $(C_6H_3Br_2CO_2)_2Ba + 6\frac{1}{2}H_2O$, is easily soluble in water and weak spirit, and crystallises in broad colourless needles. The *potassium-salt* crystallises in long needles. The *lead-salt* crystallises in small sparingly soluble needles, containing 5 mols. of water.

Together with the β-acid there are formed a *tribromobenzoic acid*, which crystallises in colourless needles melting at 178°, and a *dibromosalicylic acid*, which crystallises in colourless needles, melting at 221°, and colours ferric chloride a deep violet.

Parametabromo-nitrobenzoic Acid.—This acid is produced by the action of nitric acid on parametabromobenzoic acid melting at 229°. It forms delicate colourless needles, which melt at 162°. When treated with tin and hydrochloric acid it yields:—

Parametabromamidobenzoic Acid, $C_6H_2Br_2.NH_2.COOH$.—This substance forms colourless needles melting at 225°. Its diazo-compound gives with hydrobromic acid a *tribromobenzoic acid* which crystallises from alcohol in small colourless needles, melting at 195°, and forms a *barium salt* crystallising with 5 mols. of water.

Together with these two acids there is formed a *dibromosalicylic acid*, $C_6H_2Br_2(OH)COOH$, crystallising in colourless needles and melting at 218°. Its solution colours ferric chloride violet.

The *dibromobenzoic acid* produced by converting orthobromonitrobenzoic acid into amido-acid, and replacing the NH_2-group in the latter by bromine, crystallises in colourless needles melting apparently at 150°.

When parabromobenzoic acid melting at 248—251° is converted successively into parabromonitrobenzoic acid and parabromamidobenzoic acid, and the bromine in the last is then replaced by hydrogen, the product is a metamidobenzoic acid which crystallises in needles melting at 173—174°. It forms a very soluble barium salt with 4 mols. of water, a beautiful green copper salt, and a hydrochloride crystallising in needles.

The same parabromobenzoic acid yields a crystalline *chloride*, $C_6H_4Br.COCl$, and, through the latter, an *anilide*, $C_6H_4Br.CO.NH.C_6H_5$, crystallising in colourless laminæ which melt at 197°.

Dibromosalicylic Acid.—This substance, produced by the action of bromine on salicylic acid, forms colourless needles which dissolve sparingly in water, easily in alcohol, and melt at 219°. Its solution is coloured violet by ferric chloride. The barium, lead, and ammonium salts have been examined. Neither this acid nor monobromosalicylic acid appear to form dibasic salts.

Tribromobenzoic Acid, $C_6H_2Br_3COOH$, obtained by acting on metamidobenzoic acid with bromine, and replacing the NH_2-group in the resulting tribromamidobenzoic acid by hydrogen, melts at 186·5°. It crystallises in needles and dissolves only slightly in water. The *barium salt* crystallises with 5½ mols. of water. J. R.

Orthazobenzoic Acid. By PETER GRIESS (*Deut. Chem. Ges. Ber.*, 1868—1871).—The author has prepared orthazobenzoic acid, and finds in opposition to the statement of Claus and Fittica, that both the acid and its salts differ essentially from their respective isomerides. The acid is soluble in cold, very easily soluble in hot alcohol, and crystallises from this solution on cooling in slender dark-yellow needles; it is somewhat soluble in ether, slightly in water, but insoluble in benzene. It melts at 237°.

Barium orthazobenzoate crystallises in two distinct forms, viz., in bright yellow shining needles, of the composition $C_{14}H_8N_2O_4Ba.9H_2O$, and in large pale yellow prisms, $C_{14}H_8N_2O_4Ba.7H_2O$. This salt, in both modifications, is freely soluble in hot water, but almost insoluble in alcohol.

Silver orthazobenzoate, $C_{14}H_8N_2O_4Ag_2$, occurs as an amorphous, orange-coloured precipitate.

In the preparation of the orthonitrobenzoic acid necessary for the above investigation, the author has employed Gerland's method, which he finds to yield the acid in the proportion of 17·4 per cent. of the weight of benzoic acid employed. C. F. C.

Nitrosalicylic Acids. By H. Hübner (*Deut. Chem. Ges. Ber.*, x, 1697—1702).—1. *Mononitro-salicylic Acids.*—In former papers (*Deut. Chem. Ges. Ber.*, vii, 1320; viii, 1215) the author has shown that salicylic acid yields two nitro-derivatives melting at 280° and 145°; these bodies he now calls α- and β-nitrosalicylic acids.

α-Nitrosalicylic acid yields a diethyl-compound, which, by treatment with alcoholic ammonia, is converted into

α-Orthamidometanitrobenzoic acid, $C_6H_3.NH_2.NO_2.COOH$.—This substance forms very long delicate golden-yellow needles, melting at 263°. Its *barium salt* forms brownish-yellow crystals. The *potassium* and *lead salts* have also been examined. The acid is converted by treatment with nitrous acid into a white diazo-compound, and this, when treated with alcohol, yields a metanitrobenzoic acid which melts at 140°, and is converted by reduction with tin and hydrochloric acid into an amido-acid melting at 173°. Hence the nitro-group in the acid occupies the meta-position in relation to the carboxyl-group, as the name implies.

Together with the foregoing amidonitrobenzoic acid, there is formed an *amide*, $C_6H_3.NO_2.NH_2.CONH_2$, which crystallises in long colourless sparingly soluble needles melting at 225°. Solutions of this substance produce a deep-red colour with ferric chloride. It forms colourless compounds with nitric and hydrochloric acids.

β-Nitrosalicylic acid, when pure, melts at 131°, not at 145°, as stated in former papers.

β-Orthamidometanitrobenzoic acid, obtained in the same manner as the α-compound (see above), forms long yellow needles melting at 204°, and volatilises easily with steam. It is converted by treatment with nitrous acid and alcohol into metanitrobenzoic acid melting at 142°, and yielding, by reduction with tin and hydrochloric acid, an amido-acid melting at 174°. The *amide* formed together with the nitro-acid, melts at 109°.

It is shown by the results of this investigation that in one nitrosalicylic acid the NO_2-group occupies the meta-position in relation to the carboxyl-, and the ortho-position in relation to the hydroxyl-group; whilst in the other acid the NO_2-group occupies the meta-position in relation to the carboxyl-, but the para-position in relation to the hydroxyl-group. Hence it may be said that the NO_2-groups of the two acids replace two different meta-hydrogen atoms.

2. *Dinitro-salicylic acid.*—Both the nitrosalicylic acids described above are converted by treatment with fuming nitric acid into the same

dinitrosalicylic acid, $C_6H_2(OH)(NO_2)_2COOH + H_2O$, a body crystallising in thick needles, which become turbid on drying. It is sparingly soluble in cold water, and still more so in dilute acids. The aqueous solution is coloured red by ferric chloride. The potassium salt is not decomposed by dilute hydrochloric or nitric acid. The ethyl-ether melts at 99—100°.

3. *Sulphonic acids.*—*α*-Nitrosalicylic acid is converted by heating with fuming sulphuric acid into a sulphonic acid,

$$C_6H_2(OH)(NO_2)(COOH)SO_3H,$$

the calcium and barium salts of which crystallise in hair-like needles. This acid yields by reduction the corresponding *amido-acid*,

$$C_6H_2(OH)(NH_2)(SO_3H)COOH + H_2O.$$

α-Metamidosalicylic acid, when heated with fuming sulphuric acid, yields colourless needles of the sulphonic acid,

$$C_6H_2(OH)(NH_2)(SO_3H)COOH + 3H_2O,$$

the calcium salt of which crystallises with 5 mols. of water.

J. R.

Action of Salicylic Acid on Iron. By S. BARTLARI (*Deut. Chem. Ges. Ber.*, x, 1746).—A warm solution of salicylic acid, protected from the air, attacks iron filings, evolving hydrogen and forming a greenish solution of ferrous salt, which turns red in the air, owing to oxidation. When boiled, the ferrous salt throws down flocks of a greenish basic salt, which oxidise in the air. J. R.

Amides of Phenylglyoxalic Acid. By L. CLAISEN (*Deut. Chem. Ges. Ber.*, x, 1663—1667).—In a former paper (*Deut. Chem. Ges. Ber.*, x, 429) the author showed that, in the reaction of hydrochloric acid with benzoyl cyanide to form phenylglyoxalic acid, two stages may be distinguished, the formation of phenylglyoxalic acid being preceded by that of the corresponding amide, as represented in the following equations:—

$$C_6H_5CO.CN + H_2O = C_6H_5.CO.CO.NH_2;$$
$$C_6H_5.CO.CO.NH_2 + H_2O + HCl = C_6H_5.CO.COOH + NH_4Cl.$$

In point of fact, this amide is always obtained in considerable quantity in the preparation of phenylglyoxalic acid. The author has now prepared it free from the acid by agitating benzoyl cyanide in small portions with twice its weight of strong hydrochloric acid till solution is complete, and pouring the clear liquid into water, whereupon the amide is thrown down in delicate white prisms. A simpler plan is to agitate the hydrochloric acid solution with ether, which takes up the amide and leaves it in crystals when evaporated.

The compound thus obtained—*α-phenylglyoxamide*—melts at 90—91°, dissolves easily in ether, alcohol, benzene, and chloroform, slowly in water, and has a peculiar acrid and bitter taste. It dissolves easily in dilute alkalis in the cold, without decomposition; but on warming the solution it gives off ammonia, and the liquid afterwards gives up phenylglyoxalic acid to ether.

Alkaline solutions of the amide, when treated with carbonic acid, deposit crystals of an isomeric body—β-phenylglyoxamide—which melts at 64—65°, dissolves sparingly in water, but easily in alcohol, and forms an intensely yellow solution with sulphuric acid.

An alcoholic solution of the α-amide, when dropped into dilute hydrochloric acid, deposits a snow-white powder, consisting of a third isomeride — γ-phenylglyoxamide — distinguished from the β-amide chiefly by melting at 130°. It is a tasteless inodorous substance, nearly insoluble in ether, benzene, and chloroform. Its hot saturated aqueous solution deposits after some time beautiful four-sided tables. With sulphuric acid it behaves in the same manner as the α-amide, into which it may be converted by passing carbon dioxide into its alkaline solution.

All three amides are converted into the same phenylglyoxalic acid by heating them with alkalis. J. R.

Ethers of Terephthalic Acid. By J. Berger (*Deut. Chem. Ges. Ber.*, x, 1742).—*Propyl terephthalate*, $C_6H_4(CO_2—CH_2—CH_2—CH_3)_2$, formed by the action of propyl iodide on silver terephthalate, crystallises in long white needles, which dissolve easily in hot alcohol and in ether, and melt at 31°.

The *isopropyl-ether*, $C_6H_4[CO_2—CH(CH_3)_2]_2$, obtained by a similar reaction, forms brilliant white laminæ melting at 55—56°.

Isobutyl terephthalate, $C_6H_4[CO_2—CH_2—CH(CH_3)_2]_2$, best obtained by the action of terephthalic chloride on isobutyl alcohol, crystallises in dazzling-white, fatty laminæ, which melt at 52·5°, and dissolve easily in ether.

The *normal butyl-ether*, obtained in the same manner as the last, is a colourless oil.

The following are the melting-points of the ethers of terephthalic acid hitherto prepared:—

Methyl-ether ..	140°	Isopropyl-ether..	55—56°
Ethyl-ether ..	44	Isobutyl-ether ..	52·5
Propyl-ether ..	31		

J. R.

Amaric Acid. By Th. Zinin (*Deut. Chem. Ges. Ber.*, x, 1735).—This acid, formed, together with deoxybenzoïn, by prolonged boiling of benzamarone with alcoholic potash, was at first represented by the formula $C_{42}H_{40}O_6$, but further investigation has shown that its formula is $C_{46}H_{42}O_6$. The acid crystallises from alcohol with 2 mols. of water, which it loses at 100°. At 140—150° it is converted into the anhydride, $C_{46}H_{38}O_4$—a transculent colourless resinous mass, which becomes semi-fluid below 100°, and in that state dissolves in alcohol; the solution thus formed, however, speedily changes to a pulpy mass of small crystals, the change from the amorphous to the crystalline form being attended with considerable rise of temperature. The pure anhydride melts at 140·5° and distils in small portions without decomposition. The alkali-salts of the acid are completely decomposed by heat, in presence of free alkali, in the manner indicated by the equation:—

$$C_{46}H_{38}O_4 + 4KHO = 2C_{16}H_{15}KO_2 + 2C_7H_5KO_2 + H_2.$$

Potassium pyramarate.

Pyramaric acid dissolves easily in ether, and crystallises on spontaneous evaporation of its solution in thick rhombic plates or prisms. It is easily soluble in alcohol, but sparingly in water. The acid melts at 49°, and distils in small quantities without decomposition. The alkali-salts crystallise badly.

Amaric acid is formed, as stated above, by heating benzamarone with alcoholic potash. On substituting isobutyl alcohol for ethyl alcohol in the reaction, a homologue of amaric acid—*isobutylamaric acid*, $C_{50}H_{50}O_6$—is formed. This substance dissolves readily in caustic alkalis and carbonates, forming uncrystallisable salts. The *barium salt*, $C_{50}H_{48}BaO_6 + 2H_2O$, crystallises from weak spirit in tufts of long needles. The acid is nearly insoluble in water, but dissolves easily in ether, and also in alcohol, from which it crystallises in rhombic plates. It melts at 175—179°, and is thereby converted into an amorphous anhydride, $C_{50}H_{46}O_4$, which dissolves in ether, but is speedily deposited in the crystalline form. The anhydride melts at 137° and distils without decomposition. When heated with excess of alkali, it undergoes decomposition in the following manner:—

$$C_{50}H_{46}O_4 + 4KHO = 2C_{18}H_{19}KO_2 + 2C_7H_5KO_2 + H_2.$$

The new acid thus formed melts at 172°, distils without decomposition, and crystallises from alcohol in short four-sided prisms. It is nearly insoluble in water, but dissolves freely in hot alcohol and ether, and in aqueous alkalis. The ammoniacal solution deposits the free acid when heated.

The author considers that pyramaric acid is isomeric with dibenzylacetic acid, and that it is represented by the formula,

$$C_6H_5.C_7H_7.C_2H_5.COOH,$$

whilst the homologous acid obtained from isobutylamaric acid is to be regarded as benzylisobutylbenzoic acid. J. R.

Naphthalene-Derivatives. By P. T. CLEVE (*Deut. Chem. Ges. Ber.*, x, 1722).—*α-Nitronaphthalene-sulphonic acid* is formed by the action of nitric acid on the α-sulphonic acid, but it is best prepared by acting with sulphuric acid on nitronaphthalene. It crystallises with 4 eq. of water in long straw-yellow prisms, easily soluble in water, but only sparingly in presence of sulphuric acid. The salts are readily crystallisable and of yellow colour. The *potassium salt* crystallises in large tables with $\frac{1}{2}$ eq. of water; the *ammonium salt* in needles with $1\frac{1}{2}$ eq. of water; the *silver salt* in anhydrous monoclinic prisms; the *barium* and *lead salts* with 3 eq. of water. The *ethyl-ether* melts at 101°, the chloride at 113°. The *amido-acid* is a light crystalline powder, yielding, when treated with nitrous acid, *α-diazonaphthalic acid*, $C_{10}H_6N_2SO_3$. This last crystallises in yellow needles; when heated with water it is converted into *α-dioxynaphthalane*, $C_{10}H_6(OH)_2$, a crystalline substance, alkaline solutions of which absorb oxygen and turn brown.

β-Nitronaphthalene-sulphonic acid is formed by the action of nitric acid on β-sulphonic acid. It forms easily soluble yellow needles. The salts are for the most part sparingly soluble. The *potassium* and *ammonium salts* are anhydrous; the *barium salt* contains 1 eq. of water. The *ethyl-ether* melts at 114°, the *chloride* at 125·5°. The *amide* crystallises in anhydrous tables, or in prisms with 2 aq.

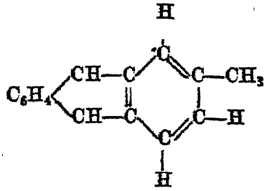
In the preparation of β-naphthalene-sulphonic acid two other bodies, *sulphonaphthalide* and *sulphonaphthalene*, are formed, as was first observed by Berzelius. The former of these, $(C_{10}H_7)_2SO_2$, is the more abundant. It crystallises in white needles, melting at 175·5°. By treatment with phosphorus pentachloride it yields *β-sulphonic chloride* melting at 212°, and a β-chloronaphthalene, $C_{10}H_7Cl$, melting at 53°, which is also formed by the action of phosphorus pentachloride on β-naphthol. The substance is, therefore ββ-sulphonaphthalide.

The author describes also two dichloronaphthalenes, distinguished as δ- and ε-compounds, obtained by distilling α- and β-sulphonic chlorides with phosphorus pentachloride. The former melts at 114°, the latter at 135°.

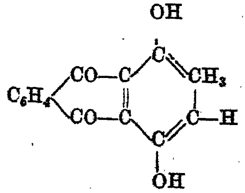
J. R.

Methylquinizarin. By R. NIETZKI (*Deut. Chem. Ges. Ber.*, x, 2011—2014).—When equal numbers of molecules of hydrotoluquinone and phthalic anhydride are heated with an excess of concentrated sulphuric acid, methyl-quinizarin is produced. This body forms a brown-red crystalline mass, with a green lustre; it is soluble in alcohol, ether, glacial acetic acid, and benzene, forming fluorescent liquids. It sublimes on heating, with partial decomposition, and melts at 160°. By distillation with zinc dust, it yields methylanthracene, convertible by oxidation with chromic acid into anthraquinone-carbonic acid, together with a large quantity of anthraquinone, a circumstance in which it agrees with the methylanthracene obtained from emodin and chrysophanic acid.

From the results above detailed, viewed in connection with the known constitution of anthracene, and the fact established by Baeyer (*Berichte*, vii, 974), that the C_2O_2 group of anthracene, occupies in both benzene-rings the position 1 : 2, it follows that methylanthracene and methylquinizarin must be represented by the following constitutional formulæ:—



Methyl-anthracene.



Methyl-quinizarin.

T. C.

Retene-sulphonic Acids. By A. G. EKSTRAND (*Deut. Chem. Ges. Ber.*, x, 1725).—Retene, submitted to the action of sulphuric acid at the ordinary temperature, forms a *disulphonic acid*, $C_{18}H_{16}(SO_3H)_2$, crystallising in easily soluble needles, with 10 aq. The salts generally crystallise in needles; the barium and lead salts are sparingly soluble. The *chloride*, $C_{18}H_{16}SO_2Cl$, crystallises in prisms melting at 175°.

A *retene-trisulphonic acid* is formed on heating retene with sulphuric acid over the water-bath. It is even more soluble than the preceding compound. J. R.

Idryl. By G. GOLDSCHMIEDT (*Deut. Chem. Ges. Ber.*, x, 2022—2030).—The idryl obtained by Bödecker (*Ann. Chem. Pharm.*, lii, 100), was a mixture of phenanthrene and pyrene. From crude idryl the author has isolated the following:—Anthracene, phenanthrene, chrysene, pyrene, and a new hydrocarbon, having the same composition as Bödecker's idryl, but different properties. The name "idryl" is retained for this body.

Analysis and vapour-density led to the formula, $C_{15}H_{10}$. Idryl melts at 110°, sublimes, crystallises in needles, and dissolves easily in benzene, carbon disulphide, chloroform, ether, and boiling alcohol, but is little soluble in cold alcohol. On slightly warming with strong sulphuric acid, it dissolves, and the liquid assumes successively a greenish-blue, a deep blue, and finally a brown colour. It yields a crystalline bromo-compound, and a compound with picric acid, the latter of which forms yellow needles melting at 184°. The quinone was also prepared; it consists of reddish-yellow needles, melting at 189°, which on heating with soda-lime yield diphenyl. T. C.

Constituents of Cinchona-bark: Cusconine and Aricine. By O. HESSE (*Liebig's Annalen*, clxxxv, 296—323).—In this paper the author gives the results of his examination of a Cusco cinchona-bark, apparently identical with that examined by Liverköhn (*Repert. Pharm.*, 33, 357), who found it to contain aricine. The bark gives off brown vapours when heated, and yields at last a brown tar, thereby differing from barks containing quinine or isomeric alkaloïds, all of which give off red vapours when heated. The author has found in the bark: aricine, a new base called *cusconine*, and a small quantity of an amorphous alkaloïd, which he believes to be derived from the other two. These bases do not exist in the bark in the free state, since they cannot be extracted by chloroform. They were isolated in the following manner:—An alcoholic extract of the comminuted bark was supersaturated with soda and shaken with ether; and the ethereal liquid was agitated with acetic acid, which took up the greater part of the alkaloïds. The acetic solution was partially neutralised with ammonia, which threw down aricine acetate, and the filtrate from this substance was then mixed with a strong solution of ammonium sulphate, whereupon the cusconine was precipitated as sulphate. The mother-liquor contained the amorphous alkaloïd, which has not been further examined. The percentage of alkaloïds contained in the bark was about 0·62 of aricine, 0·93 of cusconine, and 0·16 of amorphous substance.

CUSCONINE is thrown down from the sulphate by ammonia as an amorphous precipitate, crystallising from ether in white laminæ, and from alcohol or acetone in larger crystals. It dissolves in 35 times its weight of ether, more easily in alcohol and acetone, and very freely in chloroform, but is nearly insoluble in water. Strong nitric and sulphuric acids dissolve it with greenish coloration. A little cusconine added to a warm solution of ammonium molybdate in strong sulphuric acid colours it a dark blue, changing to olive-green when heated, and again turning blue as the liquid cools. This reaction is characteristic of cusconine and aricine. Cusconine rotates a ray of polarised light to the left; in the ethereal solution $(\alpha)_D = -27°$. The formula of the crystallised substance is $C_{23}H_{26}N_2O_4 + 2H_2O$, the water being given off at 80°. The anhydrous alkaloïd melts at 110°. It is a feeble base, forming salts which have a more or less acid reaction. The following salts have been prepared:—

Neutral sulphate, $2C_{23}H_{26}N_2O_4,SO_4H_2$. Crystallises from alcohol in laminæ. The *acid sulphate* is gelatinous and uncrystallisable.

Hydrochloride.—Not crystallisable. Forms with mercuric chloride a white pulverulent precipitate.

Platinochloride, $2(C_{23}H_{26}N_2O_4.HCl) + PtCl_4 + 5H_2O$.—Amorphous, flocculent dark-yellow precipitate.

Aurochloride.—Dirty-yellow amorphous flocculent precipitate, decomposing when warmed.

Hydrobromide.—Colourless; amorphous; soluble in water, from which it is precipitated by potassium bromide.

Hydriodide.—Pale-yellow amorphous precipitate, freely soluble in water, but sparingly soluble in solution of potassium iodide.

Thiocyanate, $C_{23}H_{26}N_2O_4.CNSH + 2H_2O$.—Pale yellow amorphous powder.

The *nitrate*, *acetate*, *citrate*, *tartrate*, *oxalate*, *thiosulphate*, and *salicylate* are all gelatinous and non-crystallisable.

ARICINE is obtained in the free state by decomposing the acetate with soda. It crystallises in white prisms, which dissolve very easily in chloroform, and less freely in ether and alcohol, but not in water. It melts at 188°, and decomposes at higher temperatures. With strong nitric and sulphuric acids it behaves in the same manner as cusconine. Its taste is slightly astringent, not bitter. In alcoholic or ethereal solution it rotates a ray of polarised light to the left. Analyses of aricine lead to the formula, $C_{23}H_{26}N_2O_4$, which is that of anhydrous cusconine. The neutral salts have a more or less acid reaction, and are partially decomposed by water. Solutions of the salts turn yellow after a time, the alkaloïd becoming converted into a coloured amorphous substance.

The *hydrochloride*, $C_{23}H_{26}N_2O_4,HCl + H_2O$, separates from its aqueous solution, on evaporation, in the form of a jelly, which afterwards crystallises.

The *platinochloride*, $2(C_{23}H_{26}N_2O_4.HCl)PtCl_4 + 5H_2O$, is an amorphous, orange-coloured precipitate, sparingly soluble in water.

The *aurochloride* is a dirty-yellow amorphous precipitate, easily decomposed.

The *neutral sulphate*, $2C_{23}H_{26}N_2O_4,SO_4H_2$, is precipitated as a white gelatinous mass, made up of delicate needles.

The *acid sulphate* is thrown down in small white prisms on adding sulphuric acid to a solution of the hydrochloride.

The *neutral oxalate* is a granular white crystalline powder.

The *acid oxalate*, $C_{23}H_{26}N_2O_4,C_2H_2O_4 + H_2O$, is precipitated by oxalic acid, from a solution of the hydrochloride. It crystallises in prisms, which soon change to rhombohedrons. The salt requires for solution 2025 parts of water at 18°, and hence affords a means of separating aricine from cusconine.

The *nitrate*, $C_{23}H_{26}N_2O_4,NO_3H$, is precipitated by nitric acid from a warm solution of the hydrochloride. It forms delicate white prisms, easily soluble in alcohol.

The *hydrobromide* is a white amorphous powder. The *hydriodide* forms small white prisms.

The *thiocyanate*, $C_{23}H_{26}N_2O_4,CNSH$, crystallises in small white prisms.

The *salicylate*, $C_{23}H_{26}N_2O_4.C_7H_6O_3 + 2H_2O$, is a pale yellow pulverulent precipitate, sparingly soluble in water, easily in alcohol.

The *acetate*, $C_{23}H_{26}N_2O_4.C_2H_4O_2 + 3H_2O$, is obtained by precipitating the hydrochloride either with sodium acetate, or with acetic acid, a reaction which distinguishes aricine from all other alkaloïds. It forms white granular crystals, very sparingly soluble in cold water. At 100° the acid is expelled, leaving the free alkaloïd.

The *acid citrate* and the *neutral tartrate* are both crystalline salts.

J. R.

Cinchonine. By H. SKRAUP (*Chem. Centr.*, 1877, 629).—The author regards Laurent's formula for cinchonine, $C_{19}N_{22}N_2O$, as correct. By fractional precipitation from alcohol of commercial cinchonine, and preparation of the tartrate, a base, probably identical with Zorn's hydrocinchonine, has been obtained. This base is oxidised by permanganate to formic acid and cinchotenine—

$$C_{19}N_{22}N_2O + O_4 = C_{18}H_{20}N_2O_3 + CH_2O_2.$$

M. M. P. M.

Alkaloïds contained in the Red Poppy. By O. HESSE (*Liebig's Annalen*, clxxxv, 329).—The milk-sap of the unripe capsules of *Papaver Rhœas* leaves on evaporation about 34 per cent. of dry residue, which the author finds to contain no trace of morphine, or any similar alkaloïd. The residue contains 2·1 per cent. of rhœadine, and traces of other, partially crystallisable alkaloïds. J. R.

Essence of Tansy. By M. BRUYLANTS (*J. Pharm. Chim.* [4], xxvi, 393—400).—Essence of tansy is a yellowish, mobile liquid, readily becoming brown when exposed to air and light; it has a strongly marked camphoraceous odour, and tastes bitter and burning, with an acrid after-taste. Its sp. gr. at 15° is 0·923, and its first boiling point, 192°, the thermometer rising soon to 204—207°, between which limits the greater part passes over; a little distillate then passes over as the temperature gradually rises to 270—280°, when a resinous mass remains in the retort, constituting about 10 per cent. of the essence employed. By fractional distillation it is not practicable to isolate any substance of constant boiling point; but by treating the essence with sodium-hydrogen sulphite, a separation of the constituents is effected, crystals of an aldehyde-compound separating, whilst a small quantity of a terpene (about 1 per cent.) can be obtained from the uncombined portion by fractional distillation over sodium; this terpene boils at 135—160°; it combines with iodine, evolving much heat, and forming a product from which much hydriodic acid is evolved on heating.

The bisulphite compound forms light, nacreous scales, insoluble in benzene and ether, soluble in dilute, but almost insoluble in strong alcohol; on heating with alcohol or water, or better with sodium carbonate solution, it is decomposed, forming a liquid readily soluble in ether and alcohol, and having the formula, $C_{10}H_{16}O$. [No analyses are quoted, though it is stated that the carbon and hydrogen agree with this formula.] The vapour-densities found in two experiments were 5·07 and 5·11 respectively, corresponding with the molecular weights, 147 and 148; the sp. gr. at 4° is 0·918, and the boiling point, 195—196°. To this substance the author applies the term *tanacetyl hydride* [*tansol* would appear to be a more convenient designation.—C. R. A. W.] When it is dissolved in alcohol, and brought into contact with 1 per cent. sodium-amalgam, a body is formed, boiling at 205—210°, which, when treated with acetyl chloride, evolves hydrochloric acid, and forms a compound ether boiling near 220°; this body forms potassium acetate on saponification with caustic potash, but does not appear to have been analysed. Bromine and iodine attack tansol, the former violently; from the products of the action of the latter, cymene was isolated, boiling at 170—175°. Hydrochloric acid gas forms a liquid compound, $C_{10}H_{16}O.HCl$, decomposed by water, with formation of hydrochloric acid and tansol. Strong sulphuric acid removes the elements of water, forming cymene and other products; the same result is brought about by heating with phosphorus pentasulphide the cymene boiling at 175—176°, and forming by the action of nitric acid an acid which melts at 176° (toluic acid), and by that of sulphuric acid and potassium dichromate an acid volatile without fusion (terephthalic acid). Phosphoric anhydride forms impure cymene, and phosphoric pentachloride gives rise to the chlorinated derivatives, $C_{10}H_{16}Cl_2$, $C_{10}H_{15}Cl$, and cymene. None of these derivatives appear to have been analysed, as no figures are quoted.

That tansol is an aldehyde is indicated by the formation of the crystalline sodium sulphite derivative, and by its giving a mirror when heated with ammoniacal silver nitrate. In a list of conclusions drawn from these results the author states that, besides the hydrocarbon, $C_{10}H_{16}$, essential oil of *Tanacetum vulgare* consists of about four-fifths of the aldehyde, $C_{10}H_{16}O$, and one-fifth of an alcohol, $C_{10}H_{18}O$, together with two resins, one acid, one without action on bases. This alcohol, he states, forms ordinary laurel camphor on oxidation. C. R. A. W.

Contributions to the Chemistry of the more important Resins, Gums, and Balsams. By ED. HIRSCHSOHN (*Chem. Centr.*, 1877, 182—183).—Galbanum and the ammonia-resins, sagapenum and opoponax, may be divided into three classes. Sagapenums, containing sulphur, and yielding by dry distillation umbellifrone, together with other products; *galbanum* and *African ammonia*, not containing sulphur, but yielding umbellifrone; and *Persian ammonia* and *opoponax*, which neither contain sulphur nor yield umbellifrone. Galbanum may be distinguished from African ammonia by its property of giving a yellowish-red or violet colour with hydrochloric acid; and Persian ammonia from opoponax by the orange-yellow colour it gives with a solution of bleaching powder.

From a good Persian galbanum light petroleum oil should extract at least 15 p.c.; from granular Levant galbanum at least 6 p.c.; and from the same variety in lumps, at least 7 p.c.

Persian and African ammonias must have 3 p.c. of soluble constituents, and Persian sagapas 15 p.c.; that from the Levant 16 p.c., and lastly, opoponax 1 p.c. After the solutions are evaporated and heated to 120°, the residue, in the case of galbanum and ammonias, should not exceed 1 p.c.; that of Persian sagapenums 5 p.c.; that of Levantine sagapas, 12 p.c.; and that of opoponax 3 p.c. of the weight of the drug, that is, the light oil should extract from galbanum and ammonias only ethereal oil, and from the remainder also resinous substances. The reactions of a large number of resins, &c., are said to be described in the original paper (*Pharm. Zeitschr. f. Russland*, xvi, 1), from an extract of which the above facts are drawn. W. R.

Chemical Compounds contained in Liquid Storax. By WILHELM v. MILLER (*Liebig's Annalen*, clxxxviii, 184—216).—The first part of the paper is historical, and the following references (in order) are made to the literature of the subject—in addition to a previous communication of the author (*Deut. Chem. Ges. Ber.*, ix, 274):—*Liebig's Annalen*, lix, 316, and liii, 321; *Annales de Chimie*, xxvi, 203; *Journal d. Pharm.* [2], xiii, 149; *Liebig's Annalen*, xxxi, 267; *J. pr. Chem.*, xxxvii, 281; *Jahresbericht f. Chem.*, 1849, 451; *Liebig's Annalen*, lv, 1; xcix, 376; clxiii, 123; clxxiii, 10; *J. pr. Chem.*, xxiii, 321; *Liebig's Annalen*, liii, 292; *J. pr. Chem.*, xxxvii, 281; *Compt. rend.*, xxi, 1376; *Liebig's Annalen*, xcvii, 185; *Jahresbericht f. Chem.*, 1860, 303; *Liebig's Annalen*, cxxxv, 122; cxli, 181, 377; cxlii, 251, and *Suppl.*, v, 368; *Compt. rend.*, lxiii, 515, 518, 788, 834, and lxv, 465; *Deut. Chem. Ges. Ber.*, vi, 255; ix, 1339; *Liebig's Annalen*, lxx, 1 and 2; lxxv, 297; clxiv, 289; clxxii, 122; cxx, 66.

The results of the author's researches contained in the second part of the paper (too long for abstraction) show that, in addition to styrolene, cinnamic acid and styracin, storax contains—

(1.) *Phenylpropyl cinnamate* in considerable quantities.

(2.) *Ethyl cinnamate* in small quantities.

(3.) A body which smells like *vanillin*, and forms a crystalline compound with sodium bisulphite. This body melts at 65°, and may possibly be ethylvanillin. It occurs in small quantities.

(4.) A resinous body which accompanies the last in small quantities. Its composition has not been determined.

(5.) Two alcoholic bodies (α- and β-*storesin*) in very considerable quantities.

(6.) Compounds of these bodies with cinnamic acid also in considerable quantities.

(7.) A sodium compound of storesin in very small quantities.

Storesin (from storax and resina) is the name proposed by the author for the body obtained from the residue left on extracting refined storax successively with caustic soda, cold alcohol, cold petroleum naphtha, hot petroleum naphtha (using an upright condenser). It melts between 160° and 168°, and has the composition, $C_{36}H_{58}O_3$.

G. T. A.

Physiological Chemistry.

Chemical Changes in the Liver. By C. FLÜGGE (*Zeitschrift f. Biologie*, xiii, 133—171).—Lehmann's analyses of the blood flowing through the portal and hepatic veins respectively were made by methods open to so many objections, that the results he obtained cannot form the basis of any theory concerning the functions of the liver. The author therefore determined to make a series of estimations of such constituents of the blood flowing through these veins as could be estimated accurately and with certainty, viz., the water, ash, and ash-constituents. The results of these analyses agreed so closely, that whatever differences existed were plainly caused by the unavoidable minute errors of manipulation. No difference in chemical composition exists therefore so far as regards these substances between the blood of the portal and hepatic veins. Estimations were next made of the amount of water and of hæmoglobin in arterial, portal, and hepatic blood, the hæmoglobin being estimated by Preyer's spectroscopic method. No difference existed in the amount of hæmoglobin in the various kinds of blood, or in their water contents.

Recent experimenters have been unable to detect any difference between the amount of sugar, fibrin, and urea contained in the blood of the portal vein and that of the hepatic vein. It therefore follows that these constituents of the blood suffer no change in their passage through the liver, and that neither an absorption nor yet a formation of these substances belongs to the functions of that organ. By parity of reasoning, and upon the basis of the experiments recorded by the author, the water, salts, and hæmoglobin of the blood suffer no change in their passage through the liver, and therefore these substances have no relation to its activity.

Such a conclusion is not tenable. To what extent then may the blood be changed by the liver without our being able to detect it analytically?

To answer this question, two factors are needed, 1stly, the amount of change in the individual constituents of the blood which can be detected analytically; and secondly, the amount of change in the same constituents which the blood in passing through the liver constantly undergoes. Should the latter be less than the former, then the impossibility will be seen of proving analytically any change of blood in the liver.

To answer these questions, we require to know what quantity of blood passes through the liver in 24 hours. This depends upon the quantity of blood held by the organ and the rate of its flow.

With regard to the flow of the blood through the liver, nothing is at present known. It occurred to the author that by means of Vierordt's infusion method, some knowledge might be obtained. Having determined the rates of the flow of blood through a dog from the crural vein through the system to the crural artery, the flow was next determined on the same dog from a vein of the intestines or stomach through the liver. By this means the difference in the times taken to complete the circulation would equal the rate of flow through the liver. This latter equalled in time the ordinary flow of the blood from a vein through the lung to an artery. Of course these results were only proximate. The quantity of blood held by the liver may be taken at 20 per cent. of its weight.

With these data we may calculate as follows.

The change in the blood of the liver of a dog of 20 kilos. weight may be estimated as requiring 16 seconds. The blood contained in the liver is 20 per cent. of the liver's weight, and therefore 3·5 per cent. of the weight of the body, or about 140 gr. Thus in 16 seconds there flows through the liver 140 gr. of blood; in one minute about 500 grams; in an hour 30 kilo.; and in 24 hours 720 kilo. In the estimation of the water in blood, results can at the best be insured only within 0·5 per cent. This in 720 kilo. equals 3600 grams. Therefore by calculation a dog could secrete at least 3600 grams of water through the liver without our analyses of the blood detecting it with certainty. A dog of 20 kilo. weight would secrete at the most only 400 grams of bile in the 24 hours.

In like manner, in the estimation of chlorine, there is an error of 0·02 per cent. which equals in 24 hours 144 grams, whilst only 3 grams of sodium chloride are secreted in the bile during the same time; and if we distribute this 3 grams over the whole quantity of the blood, we should find in the 50 c.c. taken for analyses, differences so slight as to fall far within the limits of error of the most exact analyses.

Thus the material changes in the liver can cause only such slight changes in the composition of the blood as lie within the limits of error of our methods of investigation, so that we cannot hope by a comparison of the blood flowing to and from the liver to come to any conclusions as to the functions of that organ. F. J. L.

Action of Biliary Acids on the Alimentary Canal of Dogs. By M. Schülein (*Zeitschr. f. Biologie*, xiii, 172—192).—The bile and salts of the biliary acids, when brought into the alimentary canal, greatly increase the peristaltic action of the intestines. If the dose be large, the stomach is affected, and vomiting accompanies the diarrhœa. Finally, should the dose be very large, the action on the mucous membrane of the stomach is so rapid that violent vomiting ensues and the dose is ejected before the acids reach the intestines. The dose required by a dog of from 4—6 kilo. to produce diarrhœa is 0·5 grm. of sodium cholate, whilst 1·0—1·2 grm. produces vomiting. The action of cholic acid is the most intense, whilst taurocholic acid is more powerful than glycocholic. F. J. L.

Oxalic Acid in the Urine. By P. Fürbringer (*Chem. Centr.*, 1877, 197).—The author's observations lead to the following conclusions. 1. Oxalic acid is a normal and perhaps constant constituent of urine. 2. The quantity normally excreted appears not to exceed 20 mgrm. per day. 3. The amount of calcium oxalate which separates even after standing for 24 hours affords no criterion of the total amount of oxalate in the urine. 4. The chief solvent for calcium oxalate in the urine is acid sodium phosphate. 5. The amount of oxalic acid is diminished by taking a dose of sodium bicarbonate, and is not increased by lime water or urates. 6. There is no constant relation between a large increase of oxalic acid and the stoppage of the normal process of oxidation; neither is the elimination of the acid hindered by fever.

W. R.

Chemistry of Vegetable Physiology and Agriculture.

Elimination of Oxygen from Green Twigs under Boiled Water in Sunlight. By Jos. Böhm (*Liebig's Annalen*, clxxxv, 248—258).—The author summarises the results of his experiments on this subject as follows:—

1. When green twigs of woody plants, such as privet, are enclosed in a limited atmosphere containing oxygen, in the dark, there ensues at first a diminution, but afterwards an increase, in the volume of the enclosed gases; and this increase takes place before the oxygen present is completely absorbed.

2. The diminution in the volume of gas which takes place when green twigs are enclosed in an atmosphere containing oxygen, in feeble light, is not due to assimilation of oxygen, as in the germination of seeds rich in oil, but is caused by absorption of carbon dioxide formed in normal respiration.

3. When portions of fresh plants are enclosed in an atmosphere of carbon dioxide, there takes place at first a diminution (contrary to Saussure's statements) and afterwards an increase in the volume of the gas, due to internal respiration.

4. The absorption of carbon dioxide by fresh plants is not due to the action of cellular liquids (*Zellsaft*) exclusively, since it takes place also in twigs previously dried at 100°.

5. When fresh green shoots of privet are exposed to sunlight, under boiled water, they give off more oxygen than corresponds with the volume of air contained in them. This oxygen is for the most part derived from carbon dioxide formed in the shoots by internal respiration. In prolonged experiments the evolution of oxygen becomes slower and slower, and after 3 or 4 days ceases entirely, although the shoots still appear fresh and sound. After a week, however, the shoots begin to turn brown, and butyric fermentation sets in.

J. R.

Action of Sunlight on the Vine. By H. Macagno (*Compt. rend.*, lxxxv, 810—812).—Two rows of vines were covered in April, one with a black, the other with a white cloth. The green branches and leaves were submitted to analysis at the beginning of August. The results lead to the following conclusions:—The diminution of solar light by the black cloth prevented the production of glucose in the leaves, and tartaric acid and mineral matters were found in direct proportion to the intensity of the light. R. R.

On the Pathology of Fruit Trees. By DR. EBERMAYER (*Land. Versuchs Stationen*, xx, 392).—In the preparation of cellulose for paper pulp, the sawdust, &c., is usually digested under pressure with soda-ley, and from the alkaline liquors containing resin, &c., the soda is regained by evaporation and incineration. During this process vapours are evolved alkaline in character, and depositing sodium carbonate: these act very injuriously on vegetation in the vicinity, causing the leaves of the fruit trees of the neighbourhood to become reddish-brown, and finally black, when they die. By acting on leaves of different kinds with soda-solution of sp. gr. 1·01, the author found that similar effects are produced; humus-like matters are developed by the decomposition brought about by the alkali. It is noticeable that apple leaves are affected sooner than pear, and pear sooner than plum leaves; and that if the alkaline solution be allowed to dry on the leaves, the alkaline reaction is wholly or almost destroyed by reason of the formation of acid decomposition-products. C. R. A. W.

Nitrification by Organised Ferments. By SCHLOESING and MÜNTZ (*Compt. rend.*, lxxxv, 1018—1020).—In continuation of their previous research (this *Journal*, 1877, ii, 215), the authors show that vegetable earth will not nitrify in an atmosphere containing chloroform-vapour. Nitrification is also stopped by heating the earth for an hour to 100°. Earth so heated may afterwards be exposed to a current of air purified by ignition, without nitrification taking place. Nitrification recommences if a little vegetable mould diffused through water is applied. Oxidation of organic matter still proceeds in earth which has been treated with chloroform or heated to 100°; under these circumstances carbonic acid and ammonia are produced, but no nitric acid. A porous medium is not necessary for nitrification. Sewage, or a solution containing sugar, and the phosphates and sulphates of ammonium, potassium, and calcium, can be nitrified by passing over polished pebbles. Sewage clarified by alum and filtration, and then treated with a few particles of vegetable earth and some carbonate of calcium, may be nitrified in a closed vessel through which filtered air is conducted. When raw sewage is thus treated with air, without previous seeding with vegetable earth, the result is uncertain, as sewage contains a multitude of organisms, and in the struggle for existence the nitrifying ferment may be destroyed. Vegetable earth suspended in fresh water or in sea-water is easily nitrified by passing air through the water; the nitrification takes place equally in light or darkness. On boiling the mixture of soil and water, nitrification ceases if pure air be afterwards supplied. R. W.

Fermentation of Norwegian Fish-guano and Steamed Bone-

meal. By A. Paget (*Chem. Centr.*, 1877, 206).—As the action of these manures is too slow, and as dirty products are obtained by the action of sulphuric acid, the insoluble nitrogenous compounds are decomposed by moistening with water and urine, and leaving the mass to ferment. For 50 kilos. of manure 30 litres of urine or water are necessary; 5 kilos. of gypsum are added, and the heaps are covered with gypsum or earth to prevent loss of nitrogen. The temperature rises to above 40°, and when it begins to fall the fermentation is over.

W. R.

Purification and Utilisation of Sewage. By A. Müller (*Land. Versuchs. Stationen*, xx, 391).—Irrigation processes are viewed by the author with favour. In winter when plants hybernate, the purification is less efficacious than in spring and summer, when vegetation shows the maximum of activity. Self-purification by settling and aëration, although successful with small quantities in a laboratory, does not appear likely to give good results on the large scale; whilst precipitation processes are too costly. Irrigation must be intermittent to permit of aëration and oxidation of the deposited fœcal solid matters from time to time; and in winter this will often be impracticable, unless combined with a partial precipitation process, or unless large reservoirs be constructed.

C. R. A. W.

Analytical Chemistry.

Estimation of the Free Oxygen Dissolved in Water. By J. König and L. Mutschler (*Deut. Chem. Ges. Ber.*, x, 2017—2022).—The method proposed by Schützenberger (*Ann. Chim. Phys.* [4], xx, 351) for this purpose, by means of sodium hyposulphite, ammoniacal copper solution and indigo, cannot be recommended, on account of the considerable alteration which takes place in the strength of the standards on keeping, and also because there is no convenient and safe method for standardising these solutions. Mohr's method, by the use of an ammoniacal solution of ferrous oxide and titration of the excess with permanganate, is much more exact and requires less time.

Attempts to arrive at conclusions as to the value of a water for drinking purposes from the quantity of dissolved oxygen, led to no results.

T. C.

Estimation of Atmospheric Carbonic Acid at Tabor, Bohemia, in 1874 and 1875. By Fr. Farsky (*Chem. Centr.*, 1877, 198).—10,000 vol. air at 0° C. and 760 mm., contained vols. of carbonic acid:—

Month.	Maximum.	Minimum.	Mean.
October	3·75	3·12	3·12
November	3·91	3·17	3·42
December	3·67	3·10	3·37
January	3·77	3·22	3·43
February	3·62	3·21	3·43
March	3·75	3·15	3·43
April	3·67	3·19	3·53
May	3·59	3·19	3·55
June	3·61	3·02	3·29
July	3·09	3·15	3·31
August	4·07	3·19	3·43

The amount of carbonic acid varied during the month, and appeared to depend on the weather. North-west and south-west winds lowered the proportion, while the opposite took place with north and north-east winds. W. R.

Estimation of Carbonates in presence of Sulphites and Hyposulphites. By E. POLACCI (*Deut. Chem. Ges. Ber.*, x, 1747).—The author decomposes the carbonates by means of potassium bitartrate at a gentle heat in an ordinary carbonic acid apparatus. Carbon dioxide alone is liberated, sulphites and hyposulphites remaining undecomposed. J. R.

Estimation of Nitrogen in the Nitroglycerin of Dynamite. By SAUER and E. ADOR (*Deut. Chem. Ges. Ber.*, x, 1982—1984).—The estimation of nitrogen in the nitroglycerin of dynamite by treatment with potash gives results which are always too low, owing to the occurrence of the following secondary reaction:—$C_3H_5(O.NO_2)_3 + 3KHO = 3KNO_3 + C_3H_5(OH)_3$. Correct results can be obtained only by using Dumas' method. By this means the percentage of nitrogen in three different samples of nitro-glycerin from dynamite was found to be from 18·35 to 18·52. The calculated percentage of N in pure nitro-glycerin being 18·50 proves, therefore, that dynamite contains only trinitrin. T. C.

Volumetric Estimation of Iron in Iron Ores. (*Dingl. polyt. J.*, ccxxv, 560—561.)—Ed. Hart recommends potassium permanganate as the best reagent for titration. He heats the ore to redness in a porcelain tube, for three hours at least, in a stream of hydrogen; then cools, and adds it to boiling dilute sulphuric acid, at the same time passing a stream of hydrogen through the liquid, and titrates with permanganate in the ordinary way. Coal-gas is inapplicable, as some of its constituents absorbed by the acid act on the permanganate solution.

Some brown hæmatites, reduced by this method, yield an iron almost insoluble in the acid. Dr. T. M. Drown proposes to heat such ores in air or oxygen, to burn off carbonaceous matter before passing hydrogen over them; the iron then reduced dissolves easily. Most magnetic ores yield an insoluble portion containing iron; for such ores this method is no better than ordinary ones.

Dr. Drown dissolves iron ore in hydrochloric acid, evaporates nearly to dryness, adds a little water, and then stannous chloride from a burette. The excess of stannous chloride is estimated by adding starch and standard iodine solution. The iron solution should be tolerably concentrated and warm; the tin solution should be freshly prepared: 1 c.c. = 0·012 gram iron = 3 c.c. iodine solution. Ten assays gave a mean of 38·235 per cent.; two assays with permanganate gave 38·17, and two gravimetric determinations gave 38·14 per cent. of iron. The author made four simultaneous assays in eighty minutes, the tin solution being prepared whilst the ores were dissolving. Metallic iron dissolved in hydrochloric acid with a little potassium chlorate, the solution being evaporated to dryness nearly, is used to standardise the tin solution. A solution of iron chloride some months old, which gave 0·1024 and 0·1025 of iron per volume by precipitation with ammonia, gave 0·1017, 0·1012, 0·1010, and 0·1007. J. T.

Estimation of Phosphorus in Iron and Iron Ores (two papers). By KOSCHELT, and by CAIRNS (*Chem. Centr.*, 1877, 487).—Koschelt prepares a molybdic solution by dissolving one part of pure molybdic acid together with one part of caustic potash in six parts of water, adding, after cooling, a solution of ½ part of tartaric acid in two parts of water, followed by addition of 7½ parts of nitric acid; heating the whole to boiling and filtering while hot. About one gram of the iron is dissolved in the smallest possible quantity of nitric acid (the solution should not measure more than 50 c.c.), and the filtered liquid is allowed to flow into about 30 c.c. of the molybdic solution placed in a basin on the water-bath; after complete precipitation the whole is warmed for a short time, the precipitate is collected on a weighed filter, washed with dilute nitric acid (2 : 3) and alcohol, dried at 120—130° and weighed; it contains 1·73 per cent. of phosphorus. The process of Cairns is very tedious; it consists in precipitating the ferric phosphate with ammonia, redissolving, precipitating with ammonium molybdate, redissolving, reprecipitating, again dissolving, and finally precipitating with magnesia mixture. M. M. P. M.

Aluminium Plate as a support in Blow-pipe Work. By W. M. HUTCHINGS (*Chem. News*, xxxvi, 208 and 217).—Detailed directions for using Ross's aluminium plate; accounts of various metallic sublimates are also given. M. M. P. M.

Estimation of Reducing Sugar in Commercial Products. By A. GIRARD (*Compt. rend.*, lxxxv, 800—802).—The author determines the amount of reducing sugar by weighing the quantity of metallic copper which it will precipitate from a cupropotassic solution. The copper is rapidly washed on a filter, which is burnt in the air on a platinum boat, and this is afterwards ignited in a current of hydrogen, in order to reduce the copper oxide. The saccharose present in the products is estimated by inverting it, finding the weight of copper precipitated, and deducting from this the amount previously determined as due to reducing sugar. One gram of copper is reduced by 0·569 gram of reducing sugar; but a correction represented by $\frac{180}{171}$ has to be applied for saccharose, on account of the difference of the equivalents.

R. R.

Saccharimetry. By H. MORIN (*Compt. rend.*, lxxxv, 802—805).—The author's results go to prove the optical inactivity of the reducing sugar contained in commercial products. The slight rotatory power, which in some exceptional cases this kind of sugar may possess, is too small to affect the saccharimetrical determination of commercial sugars. R. R.

On some Quick Methods for testing Milk (*Dingl. polyt. J.*, ccxxvi, 418—421)—Ritthausen (*J. pr. Chem.*, 1877 [2], xv, 329) states that 20 or 10 c.c. of milk is diluted to 20 times its volume, and 10 or 5 c.c. of solution of copper (63·5 gr. of sulphate of copper in 1 litre) added. Then as much potash is added as is sufficient to decompose the copper salt added. The precipitate soon settles, the supernatant liquid is decanted off, and the washed precipitate is placed on a filter. The filtrate contains the sugar, which can be estimated. The precipitate contains the proteid and the fat. This latter can be dissolved out by ether, after washing with absolute alcohol, the ether evaporated, and the fat weighed. The precipitate is again washed with absolute alcohol, dried over sulphuric acid, and then at 125° for two or three hours, and weighed. The dry powdery product is then well ignited, the loss giving the quantity of proteid. Schmen of Munich uses an earthenware plate, which he heats to 100°, and then allows to cool, quickly rinses it with a little water, and then places it over a glass vessel containing some concentrated sulphuric acid. The milk, which is diluted with an equal bulk of distilled water, and contained in a kind of wash-bottle (spritz-glas) is then poured over the centre of this earthenware plate, and, to prevent evaporation, covered with a ground clock-glass. Nine to ten grams of milk are sufficient. After one or two hours the serum is absorbed by the plate, and the casein and fat can be scraped off with a horn spatula, and then placed in a weighed watch-glass. This is heated to 105° in an air-bath and weighed. The fat can be dissolved out by ether, and estimated.

A. Kaiser (*Schweiz. Landwirth. Zeitung*, from the *Milch-Zeitung*, 394) gives a method of finding the quantity of fat by means of a formula into which the sp. gr. of pure and skimmed milk, of milk-fat, and of milk-serum, enter. The sp. gr. of the serum is taken to be sp. gr. of skimmed milk, + 0·0011. The sp. gr. of fat is assumed to be the same or nearly the same in all milks. The accuracy of this method depends on the degree of skimming, and the exactness of the reading of the specific gravity. The author has invented a lactometer and a skimmer for these purposes. S.

Test for Santonin. By DAVID LINDO (*Chem. News*, xxxvi, 222).—The crystals are dissolved in strong sulphuric acid without heating, small successive quantities of a very dilute solution of ferric chloride are added, and the dish is agitated: a red colour, changing to purple, and subsequently to violet, is produced. If the quantity of santonin be very small, the ferric chloride solution should be mixed with an equal bulk of strong sulphuric acid, the mixed liquid should be added to the santonin, and heat should be applied. M. M. P. M.

Detection of Saffron. By W. STODDART (*Chem. Centr.*, 1877, 477). Very small quantities of this colouring matter may be detected by boiling with dilute hydrochloric acid, containing a strip of copper-foil with a little piece of platinum touching it, and a little sugar; the colour changes to red. Saffron is unchanged by alkalis.

M. M. P. M.

Detection, by the Spectroscope, of the Adulteration of Red Wines. By F. v. LEPEL (*Deut. Chem. Ges. Ber.*, x, 1875—1877).—The juice of the beet-root (*Beta vulgaris*) which is used for imparting colour to red wines, exhibits an absorption-spectrum characterised by two distinct bands. The author finds that a white wine to which an alcoholic infusion of the root has been added, gives this spectrum unchanged; the colouring matter present in pure red wine, which prevents the recognition of the characteristic bands of the juice of the beet when present as an adulteration, may be removed by means of tannin and gelatin (Faure's reagent, which leaves the colouring matter of the beet unchanged. Characteristic modifications of the spectrum are determined by cupric sulphate, the alkalis, and other reagents. These are carefully described by the author as affording additional evidence of the presence of beet-juice.

C. F. C.

Technical Chemistry.

Purification of Water for Boilers by Haën's and Bohlig's Processes. By FERD. FISCHER (*Dingl. Polyt. J.*, ccxxvi, 94—100).—The following are analyses of water before (I) and after (II) the purifying process by Haën's method, and III shows an analysis of water in a boiler at work:—

1 litre contains—	I.	II.	III.
Chlorine	22 mg.	78	2765
Sulphuric anhydride	55	trace	147
Nitric anhydride	42	41	1260
Nitrous acid	trace	strong	very large trace
Ammonia	slight trace	trace	trace
Organic matter	35	33	0
Magnesia	9	trace	trace
Lime	175	80	2240
Percipitated by boiling:			
Lime	141		
Or,			
$CaCO_3$	252	0	0
$CaSO_4$	83	trace	250
Na_2SO_4	11	0	0
$MgCl_2$	21	trace	trace
$CaCl_2$	0	121	4236
$NaNO_3$	66	65	1983

The barium chloride employed contained $BaCl_2$ 82·18; $CaCl_2$ 0·39;

$MgCl_2$ trace; insoluble 0·48; water 15·71; chlorides of alkali-metals 1·24. The purified water reacted neutral, and still contained some sulphuric acid, as sufficient chloride of barium had not been added. It is advisable to add sufficient lime, after the addition of the barium chloride, to make the solution alkaline, so as to prevent the chlorides, &c., from attacking the cocks and sides of boilers.

A sample from another person had the following composition before (1) and after (2):—

1 litre contains—	1.	2.
Chlorine..	142 mg.	391 mg.
Sulphuric acid	209	0
Nitric acid	63	60
Nitrous acid	trace	trace
Ammonia	,,	,,
Organic matter	47	39
Baryta	0	53
Magnesia	22	12
Lime	294	241
Precipitated by boiling:		
Lime	137	
Magnesia	trace	

One litre of purified-water showed by neutralisation that it was equivalent to 21 mg. hydrate of calcium, or 17 mg. of hydrate of magnesium. The following may be taken as the composition:—

$CaCO_3$	$CaSO_4$	$CaCl_2$	$MgCl_2$	$BaCl_2$	MgH_2O_2
245	341	33	52	0	0
0	0	477	0	72	17

The chloride of barium used had the annexed composition:—

Chloride of barium 76·75; chloride of calcium 1·86; chloride of magnesium trace; water 19·72; chlorides of alkali-metals 1·67.

The water is heated, and the chloride of barium and lime added. In three or four minutes the solution becomes clear, and the purification is perfect.

The author then deals with Bohlig's preparation, and combats at the same time the remarks of the manufacturers of this article on the Haën process. He finds the preparation called "Bohlig's Magnesia preparation," to consist of burnt magnesia. The use of it requires a considerable time for the clearing of the liquid, and carbonic acid has at times to be passed through the liquid to separate the lime. Much magnesia is introduced in this process, and altogether the author considers the Haën process to be the better, and advises, if magnesia has to be used, to employ ordinary magnesia, and not the costly preparation of Bohlig.

S.

Manufacture of Iodine. By C. C. Stanford (*Dingl. polyt. J.*, ccxxvi, 85—94).—After a short history of iodine and an account of the fluctuations of the trade in kelp and iodine, the author goes on to describe the manufacture of this latter substance. The kelp is broken up into fragments, and the soluble matter extracted by water.

This solution is evaporated, allowed to stand at 40° or 45° F., and the crystals which form are fished out. At 62° F. a hard salt, containing 50 per cent. of potassium sulphate, together with Glauber's salt and sodium chloride, is deposited. The liquid is again heated, when the kelp salt (sulphate of potassium and sodium) again forms. The liquid is again cooled, and so on. The resulting liquor is mixed with $\frac{1}{7}$ Nordhausen sulphuric acid (145° F.); oxide of manganese is added, and on distillation iodine is obtained; afterwards, on addition of more oxide, bromine comes over.

The author refers to the fluctuation in the demand for kelp in consequence of the discovery of Spanish soda and the Stassfurt salt deposits. He shows that about 0·16 per cent. of iodine is got from kelp. The quantity of iodine in the sea is as 1 : 250,000, or 1 cubic mile contains 11,072 tons. Other chemists estimate the proportion to be 1 : 30,000,000. Seaweeds possess the power of taking the iodine from the sea-water, but in different degrees, as the following table will show. They take up ten times more iodine than bromine. 100 parts of dried algæ contain—

	Sarphat.	Schweitzer.	Godechens.	Wallace.	Stanford.
Lam. digitata	0·135	—	0·625	0·4440	A. 0·4535 B. 0·2946
,, saccharina	0·230	3·880	—	0·2880	C. 0·2794
Fucus serratus	0·124	0·058	0·177	0·0565	D. 0·0856
,, nodosus	—	—	0·074	0·0396	E. 0·0572
,, vesiculosus	0·001	—	—	—	F. 0·0297
Zostera marina	0·0005	—	—	—	0·0457
Rhodomela pinnastroïdes	—	—	—	—	0·0378
Hyderix siliquosa	—	—	—	—	0·2131
Hymanthalia lorea	—	—	—	—	0·0892
Chordaria flagelliformis	—	—	—	—	0·2810
Cladophlora glomerata	—	—	—	—	—

These specimens came from Larne, Ballina, Sligo, Galway, Shetland, Tyree, Coll, Colonsay, from the Isle of Man, Denmark, &c. The first five are those from which kelp is generally made. The best is the *Laminaria digitata*, which grows on rocks and always under water. The laminariæ in general form the best source and are found thrown on the shore by storms. The rest are cut generally as they rise out of water and are poorer in iodine. The method of preparing kelp is wasteful in the highest degree. Exposed to weathering, heated too strongly in burning, and mixed with sand, the product does not contain what more careful manipulation would render certain. The author read a paper before the Society of Arts (*Chemical News*, March, 1862, p. 167) in which he describes a method of destructive distillation. The products were ammonia, naphtha, tar, acetic acid, &c., and a coke or charcoal, which gives by treatment with water the compounds of iodine and other bodies. The charcoal then left resembles animal charcoal in appearance, costs only $\frac{1}{4}$ as much, and is a good deodorizer—

	Laminaria.	Fucus.
Carbon	52·54	70·32
Phosphate	10·92	1·90
Carbonate of lime	15·56	10·35
„ magnesia	11·34	7·92
Sulphate of lime	—	1·93
Alkalis	5·70	1·84
Alumina	3·94	5·74
	100·00	100·00

S.

Decomposition of Soda-waste for the Production of Sulphur. By CARL KRAUSHAAR (*Dingl. polyt. J.*, ccxxvi, 412—418).—Schaffner's method (*Dingl.* 1869, cxcii, 308, and cxciii, 42) is to throw the residue in heaps, and after leaving it some months, to strew these heaps about, whereupon chemical action sets in. The author has in this paper followed out this chemical action, and for this purpose took a sample, 1 yard below the surface of the heap, and treated 1·5 kil. with 850 c.c. of water; 30 kil. of the same sample he made into a little heap, and after half an hour treated a second portion with 850 c.c. of water. A 3rd, 4th, 5th, 6th, 7th, and 8th samples were taken at intervals of 1 hour and treated with water as before. The samples were left for 24 hours in the water and the solution contained—

	Sample No. 1.			No. 2.		
	Polysulphides of calcium.	Sulph-hydrate of calcium.	Thiosulphate of calcium.	Polysulphides.	Sulph-hydrate.	Thiosulphate.
First quantity	5·6	84·9	9·5	21·6	67·9	10·5
After ½ hour	33·0	48·2	18·8	34·0	50·2	15·8
„ 1½ „	—	—	—	40·2	34·2	25·6
„ 2½ „	31·3	11·6	57·2	41·3	30·0	28·7
„ 3½ „	—	—	—	28·0	12·8	59·2
„ 4½ „	21·5	6·7	71·8	—	—	—
„ 5½ „	—	—	—	—	—	—
„ 6½ „	14·6	6·2	79·2	—	—	—

	No. 3.			No. 4.*		
	Polysulphides of calcium.	Sulph-hydrate of calcium.	Thiosulphate of calcium.	Polysulphides.	Sulph-hydrate.	Thiosulphate.
First quantity	—	90·9	9·1	31·3	56·0	12·7
After ½ hour	26·1	62·6	11·3	42·6	37·2	20·2
„ 1½ „	38·3	44·2	17·5	29·8	18·4	51·8
„ 2½ „	35·6	38·3	34·5	16·1	4·8	79·1
„ 3½ „	—	—	—	—	—	—
„ 4½ „	—	—	—	19·2	3·8	77·0
„ 5½ „	20·2	6·3	73·5	14·2	2·8	83·0
„ 6½ „	—	—	—	11·6	2·2	86·2

It can be seen from this that the sulph-hydrate forms the greater proportion before the air is admitted and oxidation commences. In the later stages CaS_2O_3 is the most abundant compound. This salt is probably formed as follows:—

$$CaH_2S_2 + O = H_2O + CaS_2;\ CaS_2 + O_3 = CaS_2O_3, \text{ or}$$
$$CaH_2S_2 + O_4 = CaS_2O_3 + H_2O.$$

The sulphide in the fresh soda-residue is undoubtedly CaS, but this, by the action of water, is converted into CaH_2S_2:

$$2CaS + H_2O = CaH_2S_2 + CaO.$$

When this has taken place the heap is broken up and air admitted, when the reactions already given commence. If we can stop the oxidation at such a point that the polysulphides, the sulph-hydrate, and the thiosulphate are present in such proportions as give the following reactions, we get the greatest yield of sulphur:—

$$CaH_2S_2 + CaS_2O_3 + 4HCl = 3H_2O + 2CaCl_2 + S_4, \text{ and}$$
$$2CaS_2 + CaS_2O_3 + 6HCl = 3CaCl_2 + 3H_2O + S_6.$$

If the oxidation goes beyond this, the quantity of soluble sulphur decreases, as sulphite and sulphate of calcium are formed. The quantity of sulphur in the solutions of the four samples, which were taken from different parts of the heap, and which thus show that the heaps have not a uniform composition, was as follows:—

---

* This sample was taken nearer the surface of the heap.

Percentage Amount of Sulphur.

	1.	2.	3.	4.
First quantity	3·38	3·24	2·86	2·60
After ½ hour............	3·40	3·03	3·37	2·58
„ 1½ „	—	2·96	3·08	2·55
„ 2½ „	3·31	3·00	3·06	2·73
„ 3½ „	—	3·04	—	—
„ 4½ „	3·20	—	—	2·13
„ 5½ „	3·02	—	2·72	2·19
„ 6½ „	—	—	—	2·25

When the CaS_2O_3 is present in slight excess, above the quantity shown by the above equations, the precipitation can be performed in open vats instead of being precipitated in closed vessels as in the Schaffner process. The process, as carried out at Thann, takes place in a vat 2 meters in diameter and 1·5 meter deep. The liquor passes into the vat just above the bottom, and the hydrochloric acid enters by a wooden pipe, which is so arranged that the hydrochloric acid and the liquor impinge together on the bottom of the vat. The vat is half filled with water and then heated by steam to 70°. A stirrer is set in motion, and the hydrochloric acid and liquor allowed to enter in such proportions that the mixture is slightly acid. The overflow is situated about 3 c.m. below the edge of the vat. The chloride of calcium and the sulphur pass out by this overflow. The vat is always kept full, so that any sulphuretted hydrogen that may be formed is decomposed before it rises to the surface in the sulphurous acid.

An improvement on the above process is to add sufficient water to the fresh soda-residue in an iron cylinder to allow of the action of a stirrer, and then to treat it with steam at 5 at. 90 per cent. of the sulphur can thus be brought into solution. The slime from this is allowed to dry and then broken into lumps, when oxidation rapidly sets in. The result is then treated as before. The author thinks this would spare much labour. The solution of CaH_2S_2 obtained in this way could also be applied in tanning to remove the hair from hides. It would do this in 24 hours and not harm the leather. S.

Presence of Arsenic in the Sulphuric Acid Manufactured from Arseniferous Pyrites and in the various Soda Salts Manufactured from this Sulphuric Acid. By C. Hjelt (*Dingl. polyt. J.*, ccxxvi, 174—181).—The author refers to H. A. Smith's book on the chemistry of the manufacture of sulphuric acid, and remarks that, though the quantity of arsenic in the pyrites is given, no special notice is taken of the amount of arsenic in the sulphuric acid manufactured therefrom.

1. *Arsenic in Iron Pyrites.*—The arsenic is probably present as (FeS.As), but finely diffused, as it cannot be dissolved out by the solvents for arsenide of iron. Spanish pyrites gave 0·90 per cent. of arsenic, Westphalian 0·30 per cent., and Norwegian only a trace. Smith gives the following :—

Spanish (*a*)	1·651	per cent. As_2O_3
„ (*b*)	1·745	„ „
Westphalian	1·878	„ „
Norwegian (*a*), hard	1·649	„ „
„ (*b*), soft	1·708	„ „

Richardson and Watts give in "Chemical Technology"—

Spanish	0·21 to 0·31 per cent. As
Westphalian	trace
Norwegian	——

The method employed for the determination of arsenic was fusion with fusion-mixture and nitre, and precipitation of ammonia-magnesian-arsenate.

2. Quantity of arsenic in sulphuric acid—

	Arsenic.	Present as arsenic acid.
Chamber acid	0·202 p. c.	0·040 p. c.
Acid from Glover's tower	0·331 „	0·041 „
„ Gay-Lussac's tower	0·334 „	0·132 „

The chamber acid, before employment in salt-cake manufacture, is concentrated in Glover's tower. A part of this acid goes to the Gay-Lussac tower for the purpose of absorbing the nitrous gases. These nitrous gases oxidize the arsenious to arsenic acid, and this accounts for the larger proportion of arsenic acid shown by the analyses, ($As_2O_3 + 2N_2O_3 = As_2O_5 + 4NO$). The total amount of nitric acid used in this manufacture is 1·62 per cent. of the sulphuric acid produced. Calculating according to the above equation and by the result of analysis, the loss of nitric acid due to arsenic is 3·18 per cent. of total sulphuric acid produced. Westphalian pyrites with 0·30 per cent. of arsenic used 1·32 per cent. (of nitric) of total sulphuric acid manufactured, while, as above stated, with Spanish pyrites the proportion was 1·62 per cent. Other examples are, at Freiberg, 1·7 per cent. of nitric acid; arsenic in sulphuric acid = ·05 to ·30 per cent. At Grewenbrück, 1·10 per cent. is amount used; the pyrites is poor in arsenic. At the Rhenania works in Stolberg, 1 per cent. in amount, the pyrites poor in arsenic. In a chemical works at Benel, where pyrites with 1 per cent. to 1·5 per cent. of arsenic, 1·5 per cent. to 2·0 per cent. of nitric is used. Tabulated, we have—

Nitric acid used with pyrites poor in arsenic.	Rich in arsenic.
1·32 p. c.	1·62 p. c.
1·10 „	1·70 „
1·00 „	1·5—2·0 p. c.

The last sulphuric acid chamber has the purest acid with, in case cited by author, 0·019 per cent. of arsenic. This, by concentration in pans, can be used for many purposes to which the other cannot be applied.

The passage from the fire to the Glover's tower contains a white deposit with much arsenic. The longer this passage is the purer the acid, as much arsenic is deposited. The burnt pyrites contain 0·19 per cent. of arsenic.

Arsenic in the sulphate and soda manufactured with this sulphuric acid. Smith found in the sulphate manufactured from sulphuric acid with 1·051 per cent. of As 0·029 per cent., but found none in the soda. Fresenius has found it in both. The author found the sulphate quite free from arsenic. He thinks that the arsenic goes off as chloride, and that if excess of sulphuric acid be not used, the result will be free from arsenic.

Arsenic in Hydrochloric Acid from Soda-manufacture.—The raw acid has much arsenic in it. The longer the passage from the hearth or furnace to the condensing chamber, the freer the acid is from arsenic, as it is deposited on the way. Smith found 0·691 per cent. As_2O_3 in the hydrochloric acid. Filhol and Lasassin found 0·081 per cent. As, 0·174 per cent., 0·428 per cent.; so it can be seen that quantity varies much.

Arsenic in chloride of lime made from this hydrochloric acid, none.

S.

Ultramarine. By J. PHILIPP (*Dingl. polyt. J.*, ccxxiv, 635—639).—The author notices some experiments made to ascertain if the oxygen-compounds of sulphur obtained by the treatment of blue ultramarine with acids, are essential constituents of the colour, and to ascertain the relation between blue and green ultramarine (*Deut. Chem. Ges. Ber.*, 1876, 1109; *Chem. Soc. J.*, 1875, ii, 383). He concludes that the sulphuric acid obtained by treating ultramarine with hydrochloric acid arises, in part at least, from the decomposition of pentathionic acid formed by the action of sulphurous acid and sulphuretted hydrogen upon each other. Blue ultramarine, ignited in air and well washed, gave a tolerable amount of sulphuric acid; still more was found in a sample formed on the wall of a sulphate furnace. It thus appears that this acid, found when ultramarine is treated with acids, arises in part from over oxidation, by which some of the colour is decomposed. Repeated heating with water in a sealed tube, even up to 200°, failed to remove the oxygen-compounds completely. These compounds are not essential to the constitution of blue ultramarine, for the blue variety can be obtained from the green without any change in the distribution of the sulphur.

Green may be converted into blue ultramarine by the following, besides other methods: by repeated heating with iodine in air; by heating to 140° or 160° with iodine solution; by fusing with boric acid, or by repeated evaporation with solution of this acid; by heating to 160° with water; by heating with concentrated solutions of some metallic salts. These changes find their simplest explanation in the supposition that the green ultramarine has lost sulphuric acid. When the method of heating to 160° with water is used, the blue product has the same composition and weight as the original, and the sulphur-compounds obtained on treating with acids agree exactly, whilst the water used in the tube takes up only small quantities of sodium compounds. Hence the oxidation-products obtained from ordinary blue are by no means essential to its constitution. The difference between blue and green ultramarine appears to be that the latter contains a little sodium sulphide, mechanically or chemically, which hides its colour; on removing this the blue colour appears. On fusing blue ultramarine with sodium sulphate and charcoal, the green substance is obtained.

Green ultramarine boiled with zinc sulphate solution increases in volume and becomes blue, zinc being taken up by the mass and much sodium passing into the solution. Blue ultramarine thus treated also takes up zinc without changing colour essentially; here sodium is not removed simply, but free silica, alumina, and zinc oxide, removable by alkalis, are found. J. T.

Testing of Portland Cement. (*Dingl. polyt. J.*, ccxxv, 565 570).—Dyckerhoff (*Journal für Gasbeleuchtung*, 1877, 75) shows that the seven days' test of Portland cement is untrustworthy, and that the 28 days' test, though better than the first, does not indicate the binding quality of the cement when mixed with sand. From results obtained by adding four parts of sand to various cements, and determining the tenacity of test-pieces after one, two, four and twelve weeks, he recommends, as the best test, to add a considerable amount of sand and test after 28 days. For good results the well burnt cement must be finely ground.

C. Heintzel (*Notizb. des deut. Ver. für. Fabrik. von Ziegeln*, 1876, 199) concludes generally that: 1. Portland cement of proper composition becomes gradually harder, either in air or water. All oscillations in the tenacity of test pieces are due to faults in their preparation.

2. The greater the amount of water used, the less the tenacity of the product.

3. The finer the grain, the greater the tenacity.

4. Of pure cements of the same grain, those which have the greatest tenacity will give similar results when mixed with sand.

5. The coarser the sand used, the greater will be the tenacity of the *béton* produced.

5. The tenacity can be determined after seven days by Michaëlis' absorption method, either for pure cement, or for mixed cement and sand.

The specific gravitiy, determined by Seyer and Aron, ranges from 2·99 to 3·08.

The best method of testing is still an open question. J. T.

Formation of Manganiferous Iron in Blast Furnaces. (*Dingl. polyt. J.*, ccxxvi, 53—55).—Ward compares the Austrian with the American processes. At Reschitza 1·37 tons (1400 k.) of manganese ores gave ·984 cwt. (50 k.) of manganiferous iron, 35 per cent. being manganese.

The 1·37 tons contain 37·2 per cent. of Mn_2O_3, or 25·89 per cent. of manganese = 362 k. (7·12 cwts.).

The amount of manganese which passed into the manganiferous iron was ·344 cwt. (17·5 k.).

This shows that 95·5 per cent. of manganese passes into the slag. The following is the composition of the mixtures fused in Austria:—

For production of manganiferous iron with 25 per cent. of Mn	15 per cent. limestone. 85 per cent. manganese ores.
For production of manganiferous iron with 29 per cent. of Mn	28·6 ,, 71·4 ,,
For production of manganiferous iron with 35 per cent. of Mn	43 ,, 57 ,,

The slag having a composition in the last case of—

Silica	23·1
Lime	33·5
Hydrate of manganese	25·7
Oxide of iron	11·6
Alumina	6·1
	100·00

The fluidity of slag depends on the amount of manganese in it, but on the other hand, if the slag be stiff, particles of manganiferous iron become enclosed, and so the loss is the same. In America, Ward has obtained better results in a furnace 10·5 meters high, and with a blast 76 mm. in diameter. The melting point of the slag is nearly the same as that of the metal.

After 3 months' work, 270 k. (5·3 cwt.) of ore with 35 per cent. of manganese yielded 100 k. (1·9 cwt.) of manganiferous iron with 35 per cent. (1·045 cwt.) of manganese. This shows a loss of 39·5 per cent. (·855 cwt.) of manganese, or a yield of 58·1 per cent., or 12 times as much as is obtained in Austria. S.

Uses of Manganiferous Iron. (*Chem. Centr.*, 1877, 204).—Gautier believes that the manganese acts as a reducing agent, which removes iron oxide from the metallic iron, and prevents it from becoming "hot short." Henderson, of Glasgow, discovered a process of preparing manganese-iron containing 25 to 75 per cent. of manganese, thus lowering the cost of preparing manganiferous iron. The amount of manganese required for reduction is usually 1 per cent., if added as manganese-iron; the resulting iron is extremely soft; its coefficient of elasticity is 22 to 25 kilos.; its resistance to strain, 45 kilos., and its expansion, for 200 mm., 20 to 25 kilos.

It does not become hard by tempering. The product of the resistance to strain multiplied by end-expansion is nearly 7 times that of ordinary iron, and more than twice that of hard steel. This iron is used in plating ships. Addition of 1½ per cent. of manganese to inferior iron counteracts the influence of phosphorus. Addition of 1 per cent. of manganese to cast steel gives it great resisting properties. W. R.

Chromium Crucible Cast-Steel. By S. KERN (*Chem. News*, xxxvi, 198).—Directions and receipts are given for manufacturing crucible steel from Bessemer steel, iron, chrome ore, and limestone. The product is good and the price moderate. M. M. P. M.

Electrogilding by means of Potassium Ferrocyanide. By E. Ebermayer (*Dingl. polyt. J.*, ccxxiv, 631—635).—To avoid the use of potassium cyanide baths, the author dissolves 300 grams potassium ferrocyanide, 100 grams of potassium carbonate, and 50 grams of salammoniac in 3—4 litres of water at 30° to 40° C. To this is slowly added 200 c.c. of neutral gold chloride solution containing 20 grams of gold; after boiling about 30 minutes, and leaving the solution to cool, the liquid is filtered and made up to 5 litres. To increase the conductivity and to prevent the separation of iron oxide at the anode, a little potassium cyanide is added. When about 0·4 of the gold has been deposited, the bath is renewed by adding a second 200 c.c. of gold-solution and proceeding as at first; this can be repeated three or four times, after which it is necessary to add about 30 grams of ferrocyanide and the same proportion of the other salts. This renewing is repeated as long as good results are obtained. The gold from spent liquids is recovered, after filtering off any separated iron oxide, by depositing on a large copper plate totally immersed as cathode.

With the same current a warm bath gives a more copious deposit than a cold one. From many experiments the author concludes that, in a bath rich in gold, very little of the anode is dissolved, whilst the latter is more strongly attacked in a poor bath, so that a platinum anode may be used with a rich bath. J. T.

New Method of recovering Gold from Toning Baths. By Fr. Haugh (*Chem. Centr.*, 1877, 201).—The liquid is filtered into a flask of white glass, made alkaline with sodium bicarbonate, and coloured deep red with solution of aniline red. On exposure to light for 6 or 8 hours, the gold not used in toning is precipitated as a violet powder. The supernatant fluid is poured off, and when a sufficient quantity of the powder has been collected, it is transformed into gold chloride.

W. R.

Drawing of fine Platinum Wires. By A. Gaiffe (*Compt. rend.*, lxxxv, 625).—The author has so arranged an apparatus for drawing fine platinum wires, that they are protected from contact with any particles of dust that may be floating in the air. This permits of wires only $\frac{1}{47}$ of a millimeter in diameter, to be drawn without rupturing at the draw-hole, an effect traced to the contact of foreign matters. R. R.

Purification of Coal-gas. By H. Bunte (*Chem. Centr.* 1877, 185—192).—1. The ammonia existing in the gas-water is too dilute to be used with profit for purifying the gas. It does not contain enough NH_3 to absorb CO_2 and H_2S, even though acid salts were formed. This is, however, not the case, as the temperature of the water is so high as to decompose any acid salt that might be formed. The "regenerating" of dilute gas-water involves an amount of fuel disproportioned to the impurities it absorbs; consequently (2), a strong ammoniacal liquor, prepared by known methods, should be used; the strength of this liquor should be about 36·21 grams, or 47·46 litres NH_3 per litre of liquor; it then absorbs 39·2 grams, or 19·8 litres of CO_2, and 14·8 grams or 9·7 litres of H_2S. By Hill's recovery process

$\frac{4}{5}$ of the carbonic acid and $\frac{3}{4}$ of the sulphuretted hydrogen are removed from the liquor, which is passed over iron oxide to free it completely from sulphuretted hydrogen. The liquor intended for the purification of the gas is not to be allowed to mix with the gas liquor.

W. R.

Purification of Gas. By H. SCHWARZ (*Dingl. polyt. J.*, ccxxvi, 307).—The author suggests a centrifugal machine for the separation of tar from gas. A fan with sieve-like vanes revolves at high speed. The gas enters at the centre of the case surrounding the fan and passes out at the opposite side. The globules of tar are broken by the wires of the sieves and the tar is thrown to the periphery, where it agglomerates into liquid tar. The gas passes out at centre on opposite side to the entrance to avoid the sucking-in of gas, which would result if the gas were allowed to escape at the periphery. S.

Two Methods of getting Sugar from Molasses. By H. SCHWARZ (*Dingl. polyt. J.*, ccxxvi, 182—193 and 404—412).—The amount of molasses yearly produced in Europe from beet-root is very great. The author reckons that 250,000 tons of molasses are yearly produced, and this is equivalent to 125,000 tons of crystallisable sugar. He considers this equivalent to a loss of £265,000 yearly. Several chemists have tried to attack this question, some by endeavouring to precipitate a compound of sugar with lime, baryta, and strontia; others by endeavouring to get rid of the impurities which prevent the sugar from crystallising. The former methods are costly, and the latter cause much loss. The best method under the latter plan is that of osmose proposed by Dubrunfaut. Warm pure water and concentrated solution of molasses are dialysed through parchment paper. Some of the molasses goes to the water and some of the water to the molasses. The chief part of the salts and a small quantity of sugar pass into the water, and the remaining solution contains the sugar in a crystallisable state. 15 per cent. of the molasses is thus made useful as crystallised sugar.

Dr. Stammer saw that the difference of sugar and salt in dialysing power was not sufficiently great to give good results, and he proposed the addition of lime to the molasses, so as to make its passage through the parchment more difficult. The author, by means of a dialysing apparatus (see *Dingl. polyt. J.*, 1875, ccxviii, 218), has made many experiments on this method.

(1.) *Dialysis of pure Sugar.*—100 grams of loaf-sugar were dissolved in 0·5 litre. As 400 c.c. = 80 grams of sugar in the apparatus, 460 c.c. were employed outside. After 16 hours there were 540 c.c. with 60·75 grams sugar inside, and 320 c.c. with 19·20 grams of sugar outside. In this time, therefore, 19·20 grams of sugar or 24 per cent. had passed through the parchment. The size of paper was 1388 q.c. In 1 q.c. ·9 mg. of sugar passed per hour.

(2.) *Pure Sugar with Lime.*—To 67·2 grams of sugar 7·168 grams of lime were dissolved, or 3 eq. of sugar to 2 eq. of lime. 320 c.c. of sugar solution were put in the centre of apparatus, and 440 c.c. of water outside. After 18 hours there was in the centre part of the apparatus 58·05 grams sugar in 460 c.c. of solution; outside 320 c.c. with

6·750 grams of sugar. Inside there was 6·025 CaO; outside ·432 gram of CaO, 11·8 per cent. of sugar diffused, and 1·7 per cent. of lime.

For 1 q.c of parchment 0·02 mg. diffused.

(3.) *Molasses from a Sugar refinery* was dissolved in water, and lime added and filtered. A portion after separation of lime gave 24·15 per cent. of solid matter, or 15·01 per cent. of sugar, so that of the solid substance 61·3 per cent. was sugar. The percentage of salt was 22·0. After 12 hours there was—

	Solid matter.	Sugar.	Sugar quotient.* Per cent.
Inside	17·0	11·77	69·2
Outside	*6·25*	*3·01*	*49·6*

so that the amount of sugar had relatively increased.

(5.) Molasses saturated with lime and dialysed with flowing water. The outer part of vessel was so arranged that fresh water ran through it constantly but slowly.

This flowing water was evaporated after the process was finished, and both portions were analysed:—

	Solid substance.	Sugar.	Sugar quotient.
Centre of apparatus	16·00	11·40	71·25
Outer portion of apparatus	28·00	7·0	25·00

(6.) The molasses from the inner portion dialysed again with running water:—

Inner portion	14·6	11·4	78·0

(7.) Raw molasses from Barzdorf, in Austria, Silesia, contained—

Solid matter.	Sugar.	Salt.	Sugar quotient.	Salt quotient.
78·9	43·6	10·0	55·1	23·0

(8.) 80 grams of the molasses was dissolved to 200 c.c. without lime, and placed in the inner portion of the apparatus. 400 c.c. of water in outer. After 16 hours 350 c.c. found in the inner and 250 in the outer portions:—

	Solid matter.	Sugar.	Salt.	Sugar quotient.	Salt quotient.
Inner........	10·83	6·03	1·17	55·7	19·2
Outer	8·90	4·56	1·44	51·2	31·6

Of the 80 grams of molasses with 63·12 grams of solid matter, 34·86 grams of sugar and 8 grams of salt, there were found:—

	Solid matter.		Sugar.		Salts.	
	Grams.	Per cent.	Grams.	Per cent.	Grams.	Per cent.
Inner....	39·6 =	62 7	22·00 =	63·2	4·27 =	53·3
Outer....	23·0 =	36·5	11·81 =	33·9	3·73 =	46·6

From this it may be seen that the principle of dialysing with a *neutral solution is wasteful. 33·9 per cent. of sugar has to be lost in* order to get rid of 46·6 per cent. of the salts.

(9.) The same molasses (7) was rubbed with excess of lime, and after removing the lime from a portion, the amount of solid matter, sugar, and salts was obtained. 220 c.c. of lime-molasses was dialysed with 400 c.c. of water for 16 hours. In the portion employed there were 35·69 grams of solid matter (26·60 grams sugar and 4·36 salt) :—

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* The sugar quotient is the percentage of sugar in the solid substance.

	Solid matter.		Sugar.		Salts.	
	Grams.	Per cent.	Grams.	Per cent.	Grams.	Per cent.
Inner	27·5	= 76·7	20·60	= 80	2·06	= 46·8
Outer	8·34	= 23·3	5·13	= 20	2·34	= 53·2

In this latter the sugar quotient is 74·9.

(10.) Molasses with much lime dialysed for two days with running water :—

	Solid matter.		Sugar.		Salts.	
	Grams.	Per cent.	Grams.	Per cent.	Grams.	Per cent.
Inner	63·073	= 74·5	43·713	= 90·6	3·203	= 32·6
Outer	21·527	= 25·5	4·496	= 9·4	6·615	= 67·4

The sugar and salt quotients (or percentage of sugar and salt in the solid matter) were :—

	Sugar.	Salts.
Interior..........	69·3	7·3
Outer	20·9	14·7

The product crystallised easily and well.

(11.) A similar experiment gave :—

	Solid matter.		Sugar.		Salts.	
	Grams.	Per cent.	Grams.	Per cent.	Grams.	Per cent.
Inner........	37·6	= 59·6	31·5	= 79·3	1·856	= 20·6
Outer........	25·5	= 40·4	8·2	= 20·7	7·130	= 79·4

	Sugar quotient.	Salt quotient.
Inner	83·8	5·9
Outer	32·1	86·9

(12.) An experiment in which a little more than 1 eq. of lime was added to 1 of sugar, gave :—

	Solid matter.		Sugar.		Salts.	
	Grams.	Per cent.	Grams.	Per cent.	Grams.	Per cent.
80 grams of molasses..	63·2		34·88		8·04	
Inner......	39·65	= 62·0	24·79	= 68·00	3·42	= 41·6
Outer......	24·30	= 38·0	11·66	= 32·00	4·70	= 58·4

	Sugar quotient.	Salt quotient.
Inner	62·5	13·7
Outer	47·9	40·3

(13.) The same with running water :—

Inner	77·2	3·13
Outer	30·3	89·60

(14.) The outer solution in (12) was evaporated, lime added, and dialysed with running water :—

	Solid matter.		Sugar.		Salts.	
	Grams.	Per cent.	Grams.	Per cent.	Grams.	Per cent.
Inner	41·20 =	56·2	20·120 =	89·9	5·360 =	31·4
Outer	32·06 =	43·8	2·314 =	10·1	11·400 =	68·6

	Sugar quotient.	Salt quotient.
Inner	48·8	26·6
Outer	7·2	492·0

(15.) Nothing particular.

(16.) With a large quantity of lime (as much as can be added) and dialysing with running water, the author got one of the best results. With a sacrifice of 10·5 per cent. of sugar, 65·3 per cent. of non-crystallisable sugar (Nichtzucker) and 81·6 per cent. of salt separated:—

	Solid matter. Grams.	Sugar. Grams.	Salts. Grams.
Inner	78·78	56·27	2·74
Outer	39·22	9·75	12·17

	Sugar quotient.	Salt quotient.
Inner	71·4	4·8
Outer	17·2	180·0

(17.) Nothing particular.

(18.) In order to find the amount of salt that passed out of the sugar in stated times, 200 grams of molasses (with 157·8 grams of solid matter, 87·2 sugar, and 20 grams of salts) were shaken and saturated with lime and then diluted to 350 c.c. This was dialysed, the outer solution taken away and analysed after three hours (A), then after a second three hours (B), and at end of 16 hours (C). The inner solution was analysed at the end, too:—

	Solid matter.		Sugar.		Salts.	
	Grams.	Per cent.	Grams.	Per cent.	Grams.	Per cent.
A	20·23 =	13·1	4·5 =	5·1	6·24 =	34·0
B	14·91 =	9·1	5·4 =	6·1	3·76 =	20·5
C	19·54 =	12·6	10·8 =	12·3	2·94 =	16·0
D	99·52 =	65·2	67·2 =	76·5	5·40 =	29·5

	Sugar quotient.	Salt quotient.
A	22·1	138·7
B	36·2	69·6
C	55·2	27·2
D	67·5	8·0

This shows that the salt passes out in largest quantities in the first six hours.

The author draws the following conclusions:—

(1.) The diffusion of sugar by the addition of lime is made slower.

(2.) The lime-holding molasses gains a higher sugar-quotient relative to the salt quotient by diffusion, and this result is better than when neutral molasses is dialysed.

(3.) Running water acts better than standing water.

(4.) In general 70 to 90 per cent. of the salts are successfully got rid of, with a loss of only 20 to 30 per cent. of the sugar. The remaining sugar is then in a condition to crystallise to some extent.

(5.) The sugar or molasses which passes into the outer liquid can, by evaporation and addition of lime, be again dialysed and more sugar recovered.

The success of the above experiments encouraged the author to make experiments on a larger scale. The following is a brief description of the apparatus:—A long four-sided box, lined with galvanised iron, is provided with two tubes or pipes. One conducts the molasses to the bottom of the box; the other is an overflow pipe. In this box, wedged in, are a number of cells of the following construction:—A frame of wood 80 mm. wide has a parchment sheet laid on each side. Two frames, screwed, one on each side, fasten the parchment in its place and make this box water-tight at the joints. The edges of the parchment, where they rest on the frame, are covered with linseed-meal to make it even tighter. Into this cell a tube passes through the wooden frame and allows water to enter at the top of the cell. Another pipe leads the water off from the bottom of the cell. As the dialysis goes on, the salts pass into the water which sinks, and more fresh water entering at the top, it is forced out by this pipe. The author thinks it preferable to have a series of water cells, so that as one loses in dialysing power, a new one can be put in. As a sign of the molasses being purified, the sp. gr. can be taken. The supply should be so arranged that the molasses which passes off at the overflow should have a sp. gr. of 12° to 13° B.

When the molasses is dialysed, the question is the getting rid of the lime. Von Sebor has proposed to add it to the liquor from the beetroot in the manufacture of sugar. The result is to give a bad colour to the sugars.

On evaporation the lime settles out as a slime, taking with it some of the colour of the molasses. The liquor is filtered through bone-ashes, and then evaporated to crystallisation.

The author has tried it in two or three manufactories with varying success.

In the method above described, the salt and much sugar are lost, and so, after a great many experiments, the author suggests a new plan.

The molasses is diluted with 50 to 60 per cent. of water with gentle heating. On cooling, a quantity of lime equivalent to the potassium oxide in the molasses is added. An analysis has to be made to determine this, or it may be assumed that the molasses contains 10 per cent. of soluble salts, and that 60 per cent. of this is carbonate of potassium. Sufficient sulphuric acid (diluted and cooled) is then added to precipitate a double salt of potassium and calcium. Instead of adding lime, gypsum may be used, and then only so much sulphuric acid is added as will convert the carbonate of potassium into sulphate.

Magnesium sulphate can also be used, and this promises to give good results when it can be obtained cheaply, as near Stassfurt.

The precipitate of sulphate of calcium, potassium (and in cases of magnesium), is very rich. Part of fluid is filtered off, and the rest pressed out of the precipitate. The liquor is cleared of lime by carbonic acid and heating. The liquor on being left at 40° deposits abundance of sugar-crystals.

The following are laboratory experiments:—

(1.) 400 grams of molasses mixed with 150 grams of water, 12 grams of lime dissolved in 50 grams of water added (3 per cent.), and then 40 grams (10 per cent.) of sulphuric acid in 80 grams of water added. The precipitate after pressing weighed 100 grams, and contained 16 per cent. potash, equal to 4 per cent. of molasses.

(2.) In a similar experiment in which 3·83 per cent. of potash was found.

(3.) 300 grams of molasses dissolved in 90 grams water; 39 grams of magnesium sulphate dissolved in 60 grams hot water added; and then 25·8 grams of gypsum. 71 grams of pressed precipitate was obtained. In this was found potash amounting to 3·63 per cent. of the molasses used.

(4.) 300 grams of molasses, 150 grams water, 39 grams of bitter salt, and 30 grams of gypsum. 90 grams of precipitate, with potash, equal to 4·18 per cent. of molasses.

In the Klein-Kletschkau manufactory, near Schweidnitz, experiments were carried out on the sulphate of magnesium and gypsum principle; 50 cwt. of molasses were employed. 18 cwt. of moist precipitate were obtained. From one experiment 6 cwt. of sugar were obtained. In another, owing to the temperature, although performed in a vacuum, inversion set in, and the sugar would not crystallise.

S.

Behaviour of Wool towards an Ammoniacal Solution of Fuchsine. By R. Böttger (*Chem. Centr.*, 1877, 576).—A colourless ammoniacal solution of fuchsine dyes wool red. It has been supposed that the wool causes the decomposition of a compound formed by the action of ammonia upon fuchsine; but the author's experiments showed that fuchsine is merely mechanically dissolved by ammonia; when wool is soaked in this liquid, the ammonia evaporates.

M. M. P. M.

Glazing of Paper. By C. Wurster (*Dingl. polyt. J.*, ccxxvi, 75—82, 310—316, and 381—389).—The old method of sizing or glazing paper was superseded by the method of mixing a resin soap with the pulp, and then precipitating by alum. The theoretical opinion is that a salt of aluminium with the acid of the resin is formed, and that this closes the capillary pores of the paper.

The author of this paper considers, however, from the following reasons, that this is not the correct view. When, as in the glazing process, an excess of alum is added to the resin- or fat-soap, a thick, gelatinous precipitate is obtained. This, by treatment with warm alcohol, or with ether or chloroform, yields up the resin, which can be reprecipitated by water, or recovered by evaporation of the solvent. A different result is obtained when an excess of resin-soap is used. In this case a true aluminium salt is formed, which does not yield up its resin. From this it can be seen that alumina decomposes this salt. Another proof lies in the fact that the ash before and after treatment of the glazed paper with ether is the same, free resin being alone extracted, and then the paper allows ink to run.

	Ash before treatment with	Ash after.	Substance extracted.
I........	1·68 ether	1·63	3·35
II........	2·29 „	2·19	4·72
III........	2·19 „	2·18	3·70
IV*a*	1·93 „	1·81	4·50
IV*b*	1·95 benzol	1·88	4·59
V........	1·71 ether	1·66	2·11

The author shows, too, that an ethereal solution of resin will glaze paper, but the aluminium salt remains as a powder on the surface. The alkaline salt of resin or colophonium is easily decomposed by CO_2 in water, a milk resulting. This consists of finely divided particles of resin. The addition of starch makes it less easy for the resin to agglomerate, and the action of the hydrate of aluminium or of basic sulphate of aluminium is the same.

Free resin acid, or acid of colophonium, does not glaze paper well. In summing up, the author observes that, to obtain a good result, there must be as much free resin present as possible, and to obtain this he recommends the addition of sufficient excess of alum to produce free resin and a basic sulphate of aluminium, the water having a neutral, or slightly acid reaction.

The resin used in the glazing of paper is colophony, the dry residue left in the distillation of turpentine. It consists mainly of sylvic or abietic acid, $C_{20}H_{30}O_2$. It varies from light yellow to dark brown in colour, according to the method pursued in the process of distillation. An American specimen began to soften at 54°; it retained this temperature for some time; at 55° it was softer; at 63° it formed a thick fluid. The temperature then rose rapidly to 90°, when the substance was quite liquid. Powdered colophony unites into a cake when exposed to summer heat. The sp. gr. of the resin is 1·07 to 1·08.

The art of glazing the paper consists in filling up the capillary pores of the paper with resin.

The substances chiefly used for dissolving the resin are caustic soda, crystalline carbonate, and calcined carbonate of sodium. Theoretically the solution by caustic soda is the best, as the alkali is purified by the precipitation of the carbonate of calcium during its manufacture, the latter carrying all the impurities down with it. Caustic soda, however, acts very injuriously on the paper, if it be present in excess. Calcined soda is most frequently adopted. Impurities are present to a large extent in this substance, so that not only is a chemical analysis requisite to ascertain the amount of soda in each sample, but a solution has to be made, and the impurities filtered off. Crystallised carbonate of sodium appears to be the best, but then its price is high. The author recommends manufacturers to prepare crystallised carbonate from the calcined soda. The proportion of soda to resin depends on the nature of the required product. The addition of sufficient soda to dissolve all the resin, though unnecessary, defines one limit of the quantity. The amount of soda necessary to dissolve the resin and to take up the rest mechanically is the other limit. Assuming resin to be an acid of the formula, $C_{20}H_{20}O_2$, we have this reaction—

$$2C_{26}H_{30}O_2 + Na_2CO_3 = 2C_{20}H_{29}O_2Na + CO_2 + H_2O.$$

The molecular weight of the $C_{20}H_{30}O_2$ is 302; of the carbonate, 106; and of crystallised carbonate, 286. From this we get the proportions of 100 of resin to 16·5 of anhydrous, or 45·6 of crystallised carbonate. As the resin is never pure, this becomes 40 to 41. The amount of free resin that can be taken up by the sodium salt of resin is not quite known. Müller (*Fabrikation des Papieres*, Berlin, 1877) gives the proportions as 100 of resin to 25 of soda (crystallised). The soap resulting from this contains therefore, 35 to 38·5 per cent. of free resin. The solution of the resin takes place in copper vessels.

The different methods of making the glaze depending on the different proportions of resin and soda, can be classified under two heads:—1. The production of a salt of sodium which is entirely soluble in water. This is the brown glaze. 2. The production of a resin-soap, with much free resin, which on dilution is precipitated, and gives a milky appearance to the solution. This is the white glaze.

The production of the resin-soap for the brown glaze is very simple. 40 to 42 of crystalline, or a proportionate quantity of calcined soda is dissolved in 80 to 150 litres of water, and heated to boiling. 100 k. of resin are added and broken up. As soon as the resin melts, carbonic acid is evolved. The process takes from a quarter of an hour to one hour. A specimen of the soap added to distilled water should dissolve completely. The soap is allowed to stand, and the supernatant liquid taken off. If the soap requires to be washed for the removal of some of the colour, the author suggests the solution in a little water with soda, by aid of gentle heating. The soap can be again precipitated by addition of chloride of sodium. This repeated several times removes much of the objectionable colour. For the glazing of paper of medium thickness, 5 to 6 k. of resin to 100 k. of paper are required. The soap is dissolved in water, with the addition of a little starch, and then filtered.

More important, but also more difficult, is the preparation of the white glaze. It can be prepared in three ways:—1. By treatment of the resin with a quantity of alkali insufficient to combine with it chemically. 2. Treatment with excess of alkali, but stopping the action when a certain quantity of free resin is present, and then removing the excess of alkali by skimming. 3. By production of a perfectly soluble resin-soap, and addition of free resin to it. The first and second are used in the manufactory; the third is not.

In the brown glaze the concentration plays but an unimportant part, whereas in the preparation of the white glaze it is very important. The first method is to be considered here. The view of the author that the glaze is better the more free resin it contains, makes it important to add as much free resin as possible. The amount of free resin depends on the degree of concentration of the soap. The concentration of the soap by heating over fires is recommended as an easier plan than the employment of steam, especially if the latter be of low pressure.

Good results are obtained by heating 65 litres of water by steam, adding 34 k. of soda, and then slowly 100 k. of resin. The heat being continued, carbonic acid is slowly evolved, and the operation lasts from 1 to 3 hours. The heat has to be still continued, in order to dissolve the free resin. The whole occupies from 3 to 8 hours. The soap is ready when, on being taken out on a spatula, it shows the following properties. A clear, transparent, thick liquid, without bubbles, breaking off short, and not drawing out into threads. On addition to an equal volume of hot water, it should assume a brownish, gelatinous appearance, and not show yellow stripes. A portion stirred in lukewarm water should give a milky cloudiness, but no flockiness. The soap is diluted until 1 litre of liquor contains 20 to 25 grams of resin. Where such a dilute solution cannot be used, by reason of size of machinery and vessels, this proportion may be raised to 50 grams of resin. When resin soap with much free resin is used, the difference of the result, whether dilute or more concentrated soap is used, is not very great; but if 36 to 38 k. of soda are employed in the formation of the soap, it is different. It is well to add a little starch to the soap, as it renders the suspension of the resin-milk easier. The boiler is three-fourths filled with water, and strongly heated, the starch previously suspended in lukewarm water added, and the whole stirred. Cold water is added to cool it, and then the resin-soap. It is stirred, and again heated to such a degree that the hand can be held in it. The solution is then run through a flannel sack into the glazing vessels. The glaze so obtained has a fine, milk-white colour, the amount of suspended resin being 15 to 20 per cent. The author then quotes, from Müller's book, a method in which caustic soda is employed, and says that whilst caustic soda is disadvantageous in the production of brown glaze, its advantages are great when white glaze is required. One objection to the white glaze is the fact that the resin becomes precipitated on the sides of the glazing vessel, and so large masses may get into the paper. Absolute cleanliness and frequent filtration of the solution will avoid this in a great measure.

The precipitation of the resin is the next point to be examined. Sulphate of aluminium added in excess gives free resin, a basic salt of aluminium and resin, and sulphate of sodium. Sufficient sulphate must be added to remove the alkalinity of the paper-pulp. The quantity of sulphate required to effect the above two results is best determined by experiment. For 100 parts of resin, 52·4 parts of alum are required by this reaction $6(C_{20}H_{29}O_2)Na + Al_2(SO_4)_3 = (C_{20}H_{29}O_2)_6Al_2 + (3Na_2SO_4)$. This is for the decomposition of the salt of soda only. In practice 1 k. of alum is the least quantity that is added for 1 k. of resin. This allows the excess of sulphate of aluminium to act on the resin salt first produced, thus: $(C_{20}H_{29}O_2)_6Al_2 + 2Al_2(SO_4)_3 + 3H_2O = 6C_{20}H_{30}O_2 + 3Al_2O(SO_4)_2$, a basic sulphate being the result. As a rule more alum even than this is employed. According to C. Hoffmann, 2 to 3, and even 5 k. are used. The only useful ingredient in the alum is the sulphate of aluminium, and this is obtained from several sources.

If the resin be employed as white glaze, with 20 per cent. of free resin, 2·5 k. will suffice for 100 k. of paper. In the form of brown glaze, 5 k. is required; thus the 20 per cent. of free resin, or 0·5 k., is equivalent to 3 k. of resin precipitated by the sulphate of aluminium. The action of the alumina and starch is again referred by the author as to its prevention of the agglomeration of the resin, at temperatures above its melting point, and is thus mechanical. He thinks that all the qualities of starch point in a different direction to its being of direct utility as a glaze for the paper. S.

Substitution of Chlorophyll for Copper Salts in the Preservation of Fruits and Green Vegetables. By A. GUILLEMARE (*Compt. rend.*, lxxxiv, 685—686).—In the preservation of vegetables by Appert's method, some of the chlorophyll is unavoidably destroyed. Manufacturers have therefore been induced, in order to improve the appearance of the preserved article, to restore the green colour by the addition of a salt of copper. A much more harmless and equally effective colouring agent has been obtained by the author, by dissolving the chlorophyll from parsley or other similar plant with a solution of caustic soda. From the liquid thus obtained the chlorophyll is precipitated by the addition of alum, and the "lake," after washing, is dissolved in a solution of sodium phosphate. A definite quantity of this liquid is added to the water in which the operation termed "blanchissage" is conducted; the excess of chlorophyll is quickly absorbed by the immersed vegetable, and the natural green colour of the latter is thus restored. J. W.

Technico-Chemical Communications. By H. SCHWARZ (*Dingl. polyt. J.*, ccxxvi, 305—307).—1. *Analysis of the Smoke of Virginian Cigars.*—Gas contained 12 to 12·85 per cent. of CO_2, and 4·0 to 4·76 per cent. CO. Compare Bohl (1875, ccxv, 191).

2. *Lead from Raibl*, too hard for rolling or pressing into pipes. Analysis:—Fe 0·012 per cent. Cu with Ag and Bi = 0·005 per cent. Arsenic, 0·143.

3. *Brass-colouring.*—A solution of oxide of lead in potash and red prussiate of potash is taken. The brass when dipped in receives a golden-yellow colour. On heating to 40° or 50° it becomes brown.

S.

General and Physical Chemistry.

On some Points connected with the Chemical Constituents of the Solar System. By J. H. GLADSTONE (*Phil. Mag.* [5], iv, 379—385).—The formation of the solar system by the condensation of a nebulous mass made up of many different chemical elements, will have resulted in a distribution of those elements dependent on the two following considerations:—

(1.) During the process of cooling the least volatile constituents will condense first and sink towards the centre of gravity, while the rest will arrange themselves more or less in the order of their volatility.

(2.) As was pointed out by Mr. C. J. Stoney, in an atmosphere decreasing in temperature from within outwards, the lightest molecules will be the farthest from the centre of gravity.

The most volatile elements, and those of least vapour-density, will therefore be the outermost in a hot nebulous mass. This distribution is seen to occur in the sun, where hydrogen forms the bulk of the outer atmosphere, mixed with small quantities of sodium and magnesium, while the vapour of iron is found only in a lower stratum of the sun's atmosphere, and platinum has not been detected at all.

According to the nebular theory, the planets were formed by the separation of some of the outer portion of the original mass; we should therefore expect them to contain a preponderance of the more volatile elements, and those of least vapour-density; and this is indeed the case. Of the non-metallic elements, those which are plentiful have an average vapour-density of 19·8, while those which are comparatively rare have an average vapour-density of 63; grouping the metals into four classes—plentiful, common, rare, and very rare, we find that the average vapour-densities of each class are, 37·8, 104·5, 106·7, and 122·9 respectively.

The meteoric stones which fall to the earth from interplanetary spaces show this preponderance of the lighter elements still more strikingly. There are, however, in both cases many exceptions to the rule, for instance, glucinum and lithium are both rare, while lead is very common; such exceptions may be explained by supposing these elements to have been combined with others forming compounds of greater or less volatility than themselves; thus carbon is very difficult to volatilise, but its compounds with oxygen, hydrogen, &c., are gases at the ordinary temperature.

The heads of comets emit light giving band spectra which are usually referred to carbon; the volatilised carbon of the electric lamp was also found to give these band spectra; in comets, however, the carbon is probably combined with oxygen or hydrogen. F. D. B.

The Influence of Temperature upon the Coefficients of Refraction of the Natural Sulphates of Barium, Strontium, and Lead. By A. ARZRUNI (*Jahrb. f. Min.*, 1877, 526—527).—The author considered it desirable to ascertain whether the coefficients of

refraction remained constant or varied with the temperature at which the determination was made. Three isomorphous sulphates, viz., barium sulphate, strontium sulphate, and lead sulphate were selected for the investigation; firstly, because Descloiseaux observed in them a great variation of the angle of the optical axis with the temperature, from which it might justly be inferred that any change in the coefficient of refraction could easily be determined; and, secondly, it was desirable to ascertain if isomorphous compounds with analogous optical characteristics still remained analogous to an increase of temperature. For these observations the author prepared prisms out of a barytes crystal from Dufton, a cœlestine crystal from Lake Erie, and an anglesite crystal from Monte Poni, the results of the investigations being briefly as follows, viz.:—(1.) The principal coefficients of refraction of the above-mentioned isomorphous sulphates differ from each other with the temperature, but all of them decrease with an increase of temperature. (2.) The decrease in the coefficient of refraction of the three sulphates is an analogous one, and can be expressed thus, viz., $\gamma > \alpha > \beta$. Further, γ approaches the two others, whilst α withdraws from β. (3.) With anglesite the refraction is inversely as the temperature, whilst the dispersion increases for different colours. (4.) The directions of the maximum, medium, and minimum expansion of the three compounds by heat do not stand in any relationship to the values of the directions of optical elasticity in them, or to the alteration of the velocity of light in these three directions.
C. A. B.

On the Law of Absorption and its Employment in Quantitative Spectrum Analysis. By G. Govè (*Compt. rend.*, lxxxv, 1046—1049).—The author at first alludes to the phenomena of absorption, and compares the increase and dilatation of absorption-bands "due to thickening in the absorbing medium," to the increase in the bright lines in the spectra of incandescent gases caused by increase in the temperature and pressure. He says that it is not possible to determine the absorbing power of a body, unless the coefficients of absorption are known for all wave-lengths which can be studied. He thinks, however, that the absorbing power of bodies may be determined, either by direct comparison of the curves of chromatic absorption, or by measuring the intensity of the light along the whole length of the spectrum. To use the first of these methods, he employs the absorbent in the shape of a prism, and by placing one of its plane faces against the slit, with the centre angle touching one end of it, he obtains a gradually increasing thickness of the absorbing medium throughout the whole length of the slit, any deviation being neutralised by a prism of the smallest absorbing power. When white light is passed through the arrangement described above, the spectrum shows more or less wavy shadows, representing to the eye the law according to which the coefficient of absorption of the medium varies with the wave-length of the incident light. Should the slit be divided longitudinally into two equal parts, it is easy to compare the two chromatic absorption-spectra produced. By using solar light the absorption-curves may be compared with Fraunhofer's lines. The author concludes by saying that in cases requiring great accuracy this method is not applicable. J. M. T.

Theory of the Action of certain Organic Substances in increasing the Sensitiveness of Silver Haloïds. By M. C. LEA (*Amer. J. of Sci.* [3], xiv, 96—99).—Explanations of this action of certain organic substances have been offered by Poitevin and by H. Vogel, who suggest that it is due to their affinity for the halogen. The author, however, points out that all the organic substances possessing the property in question are reducing agents, and argues that it is their affinity for oxygen which, aiding as it does the affinity of the halogen for hydrogen, determines the decomposition of the silver-salt. That this is so is proved by the fact that when pyrogallol is added to recently precipitated silver iodide, and the mixture exposed to sunlight, it exhibits a distinctly acid reaction at the end of 15 minutes. Had the first-mentioned explanation been the true one, an iodo-substitution-product would have been formed, but no acid.

Substances which have a great affinity for iodine, as potassium carbonate and starch, do not increase the sensitiveness of the silver haloïd. These facts support the views of the author, as does also the process of alkaline development, the alkali, by neutralising the acid produced, assisting the development of the image. F. D. B.

A Battery in which the Carbon Electrode is the one Attacked. By P. JABLOCHKOFF (*Compt. rend.*, lxxxv, 1052—1053).—The electricity produced by electro-magnetic machines is due to the combustion of carbon. The author has attempted to produce electricity by direct action on carbon. As carbon is not attacked by liquids at ordinary temperatures, he has constructed a hot liquid electro-chemical battery. For this purpose he uses either potassium or sodium nitrate in which ordinary coke is used as one electrode, and for the other platinum-iron, or any metal not attacked by the liquid in presence of carbon. By the addition of various metallic salts the electromotive force may be modified, the metals being deposited on the unattacked electrode. The electromotive force of the battery the author states to vary between 2 and 3 units, while the Bunsen battery gives a maximum of 1·8, and Gernet 2·1. To start the action of the battery, a piece of incandescent coke is placed in contact with the crushed nitrate, heat is produced, and the action commences. A large quantity of carbon dioxide and other gases are evolved, which the author proposes to use as a motive power. A description of the apparatus is given. J. M. T.

The Movements of Electrified Mercury. By HERMANN HERWIG (*Ann. Phys. Chem.* [2], i, 73—95).—Earlier experiments on the capillary depression of electrified mercury (this *Journal*, 1877, i, 677) had rendered it probable that the surface of the glass tube in which the mercury was contained was attacked. In the experiments here detailed the mercury contained in a capillary tube was electrified by connecting it with one pole of a Holtz machine, while the other pole was connected with the earth, sparks being meanwhile allowed to pass between the poles which were not too far apart.

When the mercury was connected with the positive pole, it rose gradually in the tube when the machine was set in motion, forming, at the highest point to which it reached, and where the surface remained for some time, a dirty ring, which was not removed by repeatedly pouring clean quicksilver through the tube; this ring held up the thread of mercury when it was no longer electrified. When, on the other hand, the mercury was connected with the negative pole of the machine, it did not rise so high in the tube, no ring was formed unless the electrification was continued for a long time, and on its ceasing the quicksilver sank immediately to its former level; this latter fact clearly shows that the cohesion of the quicksilver is diminished by electrification.

Drops of mercury placed upon a horizontal glass plate, and positively electrified, rapidly formed a ring of dirty mercury on the plate: when, however, both the plate and the metal had been carefully dried, these rings were only obtained with great difficulty. The quicksilver is therefore oxidised if water be present. That the diminution of the capillary depression is not caused by such oxidation alone is, however, shown by the fact that when two similar tubes were filled, the one with hot, dry quicksilver, the other with the same substance intentionally moistened, both tubes being closed at the top, the same phenomena were observed in each on electrification. Further, when the space above the quicksilver was filled with dry hydrogen, the same effects were produced as with air, though not so rapidly, although all chance of oxidation was removed.

When the mercury of a barometer is positively electrified in the same manner, the discharge from the upper surface being facilitated by connecting the outer surface of the glass with the ground, it appears to boil violently, and glowing particles are projected against the sides of the tube; the effect is much inferior with negative electricity.

The different action of the two electricities is explained by supposing that where a break occurs in a series of conductors, the negative electricity flows more easily, while the positive collects on the surface till a far greater tension has been attained, thus occasioning, on at length passing off, a much greater disturbance.

When the mercury is connected with the positive pole the entire vacuous space is filled with bluish-green light, which, examined with the spectroscope, is shown to be mercury light; close to the mercury meniscus a yellowish-green fluorescent light is also observed which gives an almost continuous spectrum; when connected with the negative pole the bluish-green light is less developed, while the fluorescent light fills the upper part of the vacuum. The above hypothesis explains these facts also, since the negative electricity passing more easily from the quicksilver surface, the charge would accumulate at the upper portion of the tube where its presence would be indicated by the fluorescent light, whereas the positive would be found close to the surface of the mercury.

The same explanation applies to the movement of threads of mercury in horizontal capillary tubes: it was found, for instance, that when a platinum-wire, connected with the negative pole of the machine, was placed near one end of the thread, the mercury rapidly approached the wire, whereas when it was connected with the positive pole the mercury was almost always repelled. Observations made with tubes containing threads of mercury bounded at each end by water, were attended with like results.

The results of the experiments already made are summed up as follows:—

(1.) Powerful charges of electricity diminish the cohesion of mercury more than the adhesion between mercury and glass, thus lessening the capillary depression in glass tubes.

(2.) When positive electricity at high tension escapes from the surface of mercury in glass vessels, the surface being exposed to the air, oxidation takes place, more especially when moisture is present. Negative electricity has a reducing action.

(3.) The passage of electricity (particularly positive) at high tension from mercury to glass occasions decomposition of the glass.

(4.) The three facts above mentioned are the united cause of the observed diminution of the capillary depression.

(5.) Negative electricity escapes from highly charged conductors at a less tension than positive.

(6.) When surfaces of mercury are charged with electricity, the formation of mercury-vapour is greatly facilitated. Positive electricity has by far the greatest effect.

(7.) Mercury-vapour is relatively an excellent conductor of electricity. F. D. B.

On the Specific Heat of Vapours and its Variations with the Temperature. By E. WIEDEMANN (*Ann. Phys. Chem.* [2], ii, 195—217).—In Regnault's researches upon specific heats of vapours, he determined the specific heats at high temperatures by finding the quantities of heat given up in each case in condensing the gas from two different high temperatures to the same lower temperature, the difference between the two quantities giving the specific heat between the two high temperatures. He found that the specific heat c_t at a temperature t_o might be represented by the formula $c_t = c_o + 2\alpha t$, when c_0 is the specific heat at 0° and 2α the alteration of specific heat for one degree of temperature. His method is objectionable in this: that though the amount of heat given up in each case may be large and capable of determination with only a small proportionate error, nevertheless a small error may bear a large proportion to the difference between two determinations, and so considerably affect the result. Wiedemann avoids this difficulty by using an arrangement in which he can obtain the vapours at low pressures and therefore at lower temperatures, and he observes directly the heat given off in cooling a vapour from a higher to a lower temperature. He has investigated thus the values of c_0 and α in Regnault's formula for chloroform, ethyl bromide, benzene, acetone, acetic ether, and ethyl oxide. His resulting specific heats differ from those of Regnault by from 3 to 5 per cent., but agree much more closely among themselves, the variations from Regnault's results being probably due to impurities.

He finds in general that the greater the specific heat of a liquid the greater is that of its vapour. The coefficient α is of the same order of magnitude for the liquid and its vapour, and in some cases nearly the same for the two, but it varies greatly for different vapours.

J. H. P.

The Internal Condition and Latent Heat of Vapours. By P. C. PUSCHL (*Chem. Centr.*, 1877, p. 318).—By a method independent of the second law of thermodynamics, the author deduces the general equation which holds for saturated vapours. He further shows that, in the cycle of operations upon a mixture of liquid and vapour, which consists (1), in allowing the same to expand at a constant temperature; (2), heating at the volume attained and kept constant; (3), allowing it to contract to its initial volume at this increased temperature; and (4), allowing it to cool to the initial temperature while maintaining its volume constant at this point,—the work expended is not the equivalent, but is in excess of the heat obtained. There has therefore been a gain in internal work, the quantity of which may be determined in the case of water and its vapour from Regnault's experimental data. The values of the forces which determine the volume of water vapour, under the external pressure, may easily be determined for temperatures between 0° and 200°. Respecting the function pv, the author finds that, with decreasing temperature and pressure, it does not increase indefinitely to a limiting value, but attains a maximum value at a temperature near 0° C., and then decreases. If the vapour be removed from its point of saturation by expansion at a constant temperature, the product pv is found first to increase, at ordinary temperatures, to attain a maximum value at a certain point of dilution of the vapour, and then to decrease, whereas at very low temperatures a progressive decrease from the point of saturation is observed. The deviation of diluted aqueous vapour from Boyle's law is therefore essentially different from that of ordinary gases and vapours, and is rather of the nature observed by Mendelejeff in the case of rarefied atmospheric air.

C. F. C.

Abnormal Vapour-densities. By J. GUARESCHI (*Acta. d.' Acad. d. Bologna* [3], viii, 193).—The author gives a general view of the experimental investigations which have any bearing on the question of the so-called abnormal vapour-densities. He endeavours to show that in most cases of abnormal vapour-densities a partial or total decomposition can be proved with more or less certainty, and therefore that they are not really exceptions to Avogadro's law.

T. C.

Some Properties of Boric Acid. By A. DITTE (*Compt. rend.*, lxxxv, 1069—1072).—In this paper the author has determined the heat disengaged by the hydration of boric anhydride, which he finds to be 6300 thermal units at 14° per one equivalent boracic acid to three of water. In the case of solution of the hydrated acid an absorption of heat, amounting to 3181 thermal units per equivalent, takes place on the formation of a saturated solution, the solution of the hydrous acid thus absorbing about half the heat disengaged by its hydration. The author then gives tables of the specific gravity of the acid at various temperatures, both in the hydrated and anhydrous condition; he also determines the coefficient of dilatation between 12° and 80° as 0·0014785, and between 12° and 60° as 0·0015429, and gives tables of the solubility of both kinds of acid at different temperatures. In conclusion he calls attention to the use to which this action may be put as a lecture experiment to show evolution of heat by chemical action, 100 grams of the anhydride mixed with 125 grams of water being able to melt in a few minutes an ingot of Darcet's alloy.

J. M. T.

Surface-tension of Aqueous Solutions of Alcohols and Fatty Acids. By M. DUCLAUX (*Compt. rend.*, lxxxv, 1068—1069).—The author states that, by allowing different solutions of alcohols and fatty acids to flow from a tube having an orifice of known diameter, under constant pressures, and counting the number of drops given by the different solutions, he can obtain the superficial tension of these solutions by a simple calculation. By comparing these tensions he arrives at the following result:—If solutions of different densities of alcohols or fatty acids having the same superficial tension are compared, the volume-percentages of alcohol or acid which they contain have a constant ratio independent of the tension. Thus, let x be the percentage of alcohol or acid in a liquid, the superficial tension of which $= y$, and let $x = f(y)$ be the equation representing the curve of the tensions for a given substance, then $x = k f(y)$ will be the equation of the same curve for any other substance; or, the function of y in the above expression is the same for all bodies of the same organic series, and is modified only from one to the other by the introduction of a constant coefficient, k, which characterises each body. J. M. T.

On the Capillary Angle and the spreading out of Liquids upon Solids. By G. QUINCKE (*Ann. Phys. Chem.* [2], ii, 145—194). —The author has published previous investigations upon the surface-tensions and capillary angles of liquids by different methods, but the result of one method did not agree with those of another. He has therefore adopted a direct measure of the angle of capillarity, by observing the angle between the reflections of the same ray from the two surfaces near the dividing edge. He was in this way able to make very accurate measures. The angle between the same substances was found to vary from different causes. That of a drop in contact with a glass plate was less the greater the height of fall of the drop on to the plate. This is explained by the fact that if a drop is once spread out it does not contract again properly, and so makes a smaller angle with the plate than it would otherwise. But the most important modifying cause was the greater or lesser cleanliness of the plate.

The best method of cleaning a surface was to heat it in sulphuric acid, wash it, and allow it to stand in distilled water, and then to dry it in the colourless flame of a Bunsen's burner. Upon a surface thus prepared fluids like water, alcohol, &c., seemed to spread out at once and to have a capillary angle of zero. But a few seconds sufficed for the condensation of air or moisture on the surface and a consequent alteration of the angle. The longer the surface was exposed to the air the less clean it became and the greater was the angle. The slightest trace of oil was sufficient to affect the surface, and when once present was difficult to remove. It seems probable that the angle for liquids, such as water, alcohol, &c., upon clean glass, crystal, or metal surfaces is zero, and that the liquids immediately spread out, but that when it has a different value, a layer of some substance is present upon the solid surface. This layer may be excessively thin, too thin even to show the interference colours. It may consist of foreign solid, liquid, or gaseous substances, or part of the liquid which is being investigated may itself spread out over the surface, and form a very thin layer with a different surface-tension from the rest of the liquid which may then rest upon it in a lenticular form. The presence of these layers may be proved by the so-called creeping of salts, or by their conduction of electricity. They will account for Moser's pictures (Hauchbilder).

If two liquids, miscible in all proportions, are in contact with one another and with a third solid body, they will have no definite common surface with a surface-tension, and therefore the one which has the greater surface-tension at the solid surface will be driven by the other away from the solid. By this may be explained some of the phenomena of diffusion of salts through membranes, &c. J. H. P.

Studies on Chemical Volumes. By W. OSTWALD (*Chem. Centr.*, 1877, 25—32 and 42—43).—Several attempts have been made to answer the question how two acids divide themselves towards a base in aqueous solutions. Berthelot and St. Martin adopted a chemical method (*Ann. Chim. Phys.* [4], xxvi, 433, 1872), which, however, is open to many objections. The calorimetrical method of A. Müller (*Pogg. Ann.*, Suppl. vol., vi, 123, 1875), and that of J. Thomsen, depending on the evolution of heat (*Pogg. Ann.*, cxxxviii, 65, 1869), give much more satisfactory results.

The method now proposed by the author depends on the measurement of the specific gravities of the solutions. Since alterations of volume generally take place during chemical processes in aqueous solutions, it follows that if these are different in one case from what they are in another, the relative magnitudes of action of two bodies acting simultaneously may be measured by the alteration in volume.

For instance, the sp. gr. of an equivalent of NaO* in solution is 104051, and that of an equivalent of SO_3* in solution is 102970 compared with water at 20°; hence the sp. gr. of $NaO.SO_3$ in solution should be 207021. It is found to be 205218; hence a difference of −1103. With NaO and NO_5 the difference is found to be −1868. Thus—

NaO............ = 104051 sp. gr.
NO_5........... = 103083

Sum........ 207134
$NaO.NO_5$ found .. 205266

−1868

* O = 8 : S = 16.

The difference between the contractions in the two cases amounts to −765. In this way a series of numbers is obtained which may be compared with those obtained by Thomsen by means of the formula $\frac{n}{n + 0{\cdot}8} \times 555$.

The agreement of the numbers obtained by the two methods is shown in the following table:—

	Found by author's method.	Calculated by formula.
$NaOSO_3.\frac{1}{4}SO_3$	− 129	− 132
$NaOSO_3.\frac{1}{2}SO_3$	− 213	− 213
$NaOSO_3.\ SO_3$	− 320	− 309
$NaOSO_3.2SO_3$	− 398	− 396
$NaOSO_3.4SO_3$	− 452	− 462

Thomsen's formula is $\frac{n}{n + 0{\cdot}8} \times$ const.

In other experiments Guldberg's formula (Guldberg et Waage, *Etudes sur les Affinités chimiques*, Christiania, 1867) is employed, and the results are shown to agree.

The analogy between the change of volume and evolution of heat is very striking, as in the following cases:—

	Evolution of heat.	Condensation.
$NaO.SO_3$—$NaO.NO_5$	− 2072	− 765
$NaO.SO_3$—$NaO.HCl$	− 1949	− 740
$NaO.SO_3.\frac{1}{2}SO_3$	− 631	− 213
$NaO.SO_3.\frac{1}{2}NO_5$	− 1292	− 472
$NaO.SO_3.2NO_5$	− 2026	− 748
$NaO.SO_3.2HCl$	− 1878	− 688

K. Hofmann proposed a method somewhat similar to that of the author to solve a similar question (*Pogg. Ann.*, cxxxiii, 575).

G. T. A.

Inorganic Chemistry.

The Reducing Action of Hydrogen. By D. Tommasi (*Istituto Lombardo* [2], x).—The author concludes that, for the explanation of certain reducing actions of hydrogen, it is not necessary to make the assumption of an allotropic modification of the element. In most instances a sufficient explanation is obtained if we suppose that the evolved hydrogen possesses various quantities of heat in the different phenomena observed. This supposition he endeavours to substantiate by a number of experiments.

T. C.

The Gases dissolved in Sea-water. By J. Y. Buchanan (*Chem. Centr.*, 877, 742).—The author describes the apparatus used by him for determining the oxygen, nitrogen, and carbonic anhydride on board of the "Challenger." His conclusions are, that the amount of oxygen and nitrogen in sea-water is less than that contained in river-water, but the proportion of the two elements to each other is nearly the same; that the absolute amount of gas depends on the temperature; and that water at a great depth has all the physical properties of surface water. Nevertheless the belief that water from a great depth parts with gas when relieved from pressure is true, inasmuch as bubbles appear on the side of the vessel in which it is contained, when it is allowed to stand for some time. Surface water contains 33 to 35 per cent. of its volume of oxygen; water from the Trade Winds' regions gave the first figure, and that from the Antarctic Circle the second. Water covering diatomaceous mud contains most, and covering red clay least oxygen. The amount of oxygen decreases up to a depth of 1,800 feet, and then increases. It apparently depends on the presence of animal life. W. R.

Action of Oxalic Acid on Sodium Silicate. By E. MONIER (*Compt. rend.*, lxxxv, 1053—1054).—The author introduces a solution of oxalic acid, 75 grams to the litre, into a vessel containing 500 c.c. solution of sodium silicate. The liquors do not mix, and a crust is formed at their point of contact, consisting of amorphous hydrated silica. This layer increases in thickness in certain cases, having reached 7 to 8 mm. after standing two months. The crust sets quite hard, and when heated decrepitates, giving a fine white sand hard enough to polish glass. J. M. T.

The Action of Phosphoric Acid on Calcium Carbonate. By H. RITTHAUSEN (*Land. Versuchs-Stat.*, xx, 401—407).—An aqueous solution of phosphoric acid acts on precipitated chalk, forming small needle-shaped crystals of di-calcium phosphate, $Ca_2H_2P_2O_8$; the triphosphate is never formed. The crystalline character of the phosphate renders it possible to detect very small quantities of this substance, even in presence of a large excess of calcium carbonate, by means of the microscope. The finely divided chalk contained in marl deposited in the beds of streams or ponds is easily attacked by phosphoric acid. Dense particles of calcium carbonate in marl, which are scarcely acted on by phosphoric acid, are converted into di-calcium phosphate by the simultaneous action of carbonic and phosphoric acids. W. C. W.

On the Formation of Ultramarines and their Colorations. By E. GUIMET (*Compt. rend.*, lxxxv, 1072—1074).—When ultramarine is being prepared, the mixture becomes successively coloured brown, green, blue, violet, red, and white, in the order named. These changes the author ascribes to the gradual oxidation of the mixture of kaolin, sulphur, and sodic carbonate and sulphate. The brown colour appears with the blue flames due to the combustion of sulphur, the green just after the sulphur flames have ceased, and the blue is first seen at a temperature of about 700°. If, after this point is reached, heat is still applied, and free access of air permitted, the mixture becomes violet, red or rose-coloured, and finally white. When the white ultramarine is heated to redness with carbon, the red, violet, blue, green, or brown varieties are reproduced, according to the quantity of carbon used, and these colours may again be made to pass through changes in the same order as before by further oxidation. Hydrogen, ammonium chloride, and other reducing agents act in the same manner as carbon. These facts, the author thinks, show that the changes of colour are due to different degrees of oxidation, as also that they may be due to the sulphur in the mixture, this being shown by the fact that the colours differ when other bodies of the same group are used. He thinks also that the soda, though not producing the colours directly, is necessary, since any attempt to replace it by another substance prevents the formation of the colours. He considers that several varieties of ultramarine exist, and that a further study of these bodies will be of advantage. J. M. T.

Silver Ultramarine. By J. PHILIPPS (*Deut. Chem. Ges. Ber.*, x, 2031).—The product obtained by the action of silver nitrate on ultramarine blue (p. 113 of this volume), evolves sulphuretted hydrogen when treated with an excess of hydrochloric acid; there is no action, however, with a small quantity of acid. T. C.

Oxidation of Metallic Sulphides. By PH. DE CLERMONT and H. GUIOT (*Compt. rend.*, lxxxv, 714).—If moist manganese sulphide is suddenly compressed and powdered, rapid oxidation takes place, and the temperature of the mass rises several degrees. Recently precipitated nickel and ferrous sulphides oxidise even more violently than manganese sulphide: when strongly compressed and then powdered between the fingers, the temperature of the sulphide rapidly rises through 35 or 45 degrees, and aqueous vapour is disengaged.

The sulphides of cobalt, copper, and zinc, when treated in a similar manner, do not oxidise rapidly enough to give rise to a disengagement of heat. J. W.

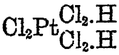
The Behaviour of Iodine to Amido-mercuric Chloride, in Presence of Alcohol; and a Safe Method of Preparing Iodide of Nitrogen. By R. BÖTTGER (*Chem. Centr.*, 1877, 651).—Although iodine may be ground in a mortar along with amido-mercuric chloride, with no other action than the formation of mercuric iodide, yet in presence of alcohol, an explosion always takes place in thirty or forty minutes, preceded by evolution of nitrogen, and sometimes separation of mercuric chloride. In presence of chloroform or amyl alcohol, gas is evolved, but no explosion occurs.

The author's process for preparing nitrogen iodide consists in treating a solution of iodine chloride, obtained by heating iodine with nitrohydrochloric acid, with ammonia. Thus prepared, it never explodes when moist, and when dry, only when touched with a piece of wood, or some similar substance. W. R.

Anhydrous Sodioferric Pyrophosphate. By S. M. JÖRGENSEN (*J. pr. Chem.* [2], xvi, 342—344).—The brownish-coloured glass, obtained by strongly heating a mixture of microcosmic salt and ferric oxide, is slowly melted in a platinum dish by the heat of a Bunsen's burner. The fused mass is treated with dilute hydrochloric acid, which dissolves out sodium phosphate, and leaves a bluish pearly crystalline residue of sodioferricpyrophosphate, $Na_2Fe^{vi}_2P_4O_{14}$. This compound crystallises in rhombic tables, and also in prisms terminated by acute pyramids; it can be recrystallised by solution in molten microcosmic salt. It is decomposed by fusion with sodium carbonate, or by boiling with strong sulphuric acid, concentrated hydrochloric or nitric acids have scarcely any action on this body. W. C. W.

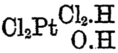
Action of Silver Nitrate on Hydroplatinic Chloride. By S. M. JÖRGENSEN (*J. pr. Chem.*, [2], xvi, 345—358).—The addition of silver nitrate in excess, to a cold solution of hydroplatinic chloride, throws down the whole of the platinum in the form of a yellow precipitate, having the composition $2AgCl.PtCl_4$. This substance has not been obtained in the pure state, as it is slowly decomposed by cold, and rapidly by hot water, into a solution of Norton's salt, $PtCl_45H_2O$ (*J. pr. Chem.*, [2], ii, 469; v, 365), and an insoluble residue, consisting of impure silver chloride.

Norton's salt loses four molecules of water at 100°, the fifth molecule cannot be expelled without decomposing the compound. The aqueous solution of this substance has an acid reaction, decomposes carbonates, and produces with silver nitrate a yellow precipitate of $Ag_2PtCl_4(OH)_2$. With ammonia, it forms a precipitate of ammonio-platinic chloride, and the filtrate yields on evaporation a black, amorphous, hygroscopic residue of platinum hydroxychloride. The relation between these bodies is shown thus:—



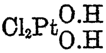
$\mathrm{Cl_2Pt}\genfrac{}{}{0pt}{}{\mathrm{Cl_2.H}}{\mathrm{Cl_2.H}}$

Hydroplatinic chloride.



$\mathrm{Cl_2Pt}\genfrac{}{}{0pt}{}{\mathrm{Cl_2.H}}{\mathrm{O.H}}$

Norton's salt.



$\mathrm{Cl_2Pt}\genfrac{}{}{0pt}{}{\mathrm{O.H}}{\mathrm{O.H}}$

Platinum hydroxychloride.

The action of silver nitrate on a hot solution of hydroplatinic chloride may be represented by the following equations:—

$$H_2PtCl_6 + 2AgNO_3 = Ag_2PtCl_6 + 2HNO_3.$$
$$Ag_2PtCl_6 + H_2O = HPtCl_4.OH + 2AgCl.$$
$$H_2O + HPtCl_4.OH + 2AgNO_3 = Ag_2PtCl_4(OH)_2 + 2HNO_3.$$

The silver salt obtained by adding silver nitrate to Norton's salt is not analogous to the acid from which it is derived, since it yields by double decomposition with ammonium chloride platinosemidiammonium chloride, $\mathrm{Cl_2Pt}\genfrac{}{}{0pt}{}{\mathrm{(N_2H_6Cl)}}{\mathrm{Cl}}$, and silver chloride. W. C. W.

Platinosoplatinic Oxide. By S. M. JÖRGENSEN (*J. pr. Chem.* [2], xvi, 344).—Platinosoplatinic oxide, Pt_3O_4, is obtained by heating one part of anhydrous sodium platinochloride with four parts of dry sodium carbonate, until the mixture begins to fuse. (The platinochlorides of potassium and ammonium cannot be substituted for the sodium salt.) The black residue which remains after treating the fused mass with water, and with dilute nitric acid, is repeatedly washed by decantation with hot nitric acid, and finally with water acidified with nitric acid, and is then dried at 110°. This oxide is converted into platinum black by formic acid; it is not attacked by mineral acids, not even by boiling aqua regia. It slowly loses oxygen at a red heat, but it is rapidly reduced in an atmosphere of hydrogen or coal gas, even at the ordinary temperature. W. C. W.

Mineralogical Chemistry.

The Growth and Twin Development of Crystals of Diamond. By J. Hirschwald (*Jahrb. f. Min.*, 1877, 520—525).—The author's independent investigations of the phenomena observed in the growth of diamond crystals, fully confirm those of Sadebeck (*Jahrb. f. Min.*, 1877, 197), proving completely that a parallel aggregation occurs in the growth of diamonds, resulting in a rectangular indentation of the octohedral edges. He further shows:—1. That there is no evidence of any penetration having taken place, all signs of such an occurrence being wanting. 2. The absence of a uniform and symmetrical development of the individual portions of the intergrown edges. 3. The common occurrence of indentations which do not differ from each other in the slightest degree. 4. The independent development of the octohedral segments occurring in the opposite octants. 5. The analogy of these peculiar developments with other well defined holohedral species, exhibiting a similar formation by aggregation. 6. The indentations observed on the edges of diamond crystals are not due to any twin-formation. Hirschwald states, therefore, that from henceforth the diamond must be considered a holohedral species. The aggregated construction of some diamonds was made very apparent by examination in polarised light, most of them exhibiting a distinct depolarising effect parallel to a trigonal axis when examined with a delicate selenite plate in the polarising apparatus. C. A. B.

Report on a Memoir by Stanislas Meunier, entitled Composition and Origin of the Diamond-bearing Sand from Du Toit's Pan (S. Africa). (*Compt. rend.*, lxxxiv, 1124—1130).—According to the report, the investigation of St. Meunier respecting the composition of the diamond-bearing sand of Southern Africa, and his deductions therefrom as to its origin, which are given in this *Journal* (1877, ii, 280), correspond in the main with the results obtained by previous geologists; at the same time the report expresses no decided opinion respecting his original proposition, viz., that the very varied rock-fragments composing the sand must have been derived from wholly different sources, and have been mechanically carried to the spot where the mixture actually took place.

A memoir was published by E. S. Dana, in 1874, on the "dry mines" of Southern Africa, in which he proves that from the disposition of the sands in vertical layers, and from the nature of their component fragments, it is scarcely possible to arrive at any other conclusion than that the diamond has had a deep-seated origin, and that it has proceeded from below upwards. In this opinion Prof. Ramsay, Prof. Forbes, and Mr. Stow, who has examined the "pans" of Griqualand West, unanimously concur.

Attention is drawn to the fact that the "vertical alluvial deposits" of the author, which are supposed by him to be closely related to the diamond-bearing sand-wells, are also closely related to the geyser deposits of Belgium, which were carefully studied by d'Halloy about 30 years ago. Further, that the angles and edges of the crystals of *carbonado*, or black diamond of Brazil, are almost invariably abraded, rounded, and even polished, which shows that they must have been submitted to energetic and prolonged attrition; that their faces are not unfrequently marked by mirror-like striæ, which seem to indicate that before arriving at the surface they had been violently pressed together against each other, probably in a manner similar to that which has often been observed in eruptive breccias, and in many conglomerates.

With respect to the rocks associated with diamonds, the specimens from South Africa differ from those of Brazil and India, in the fact that with the former quartzose rocks predominate, while with the latter magnesian rocks are chiefly found; in many deposits also, such as those of Borneo, Ural, Australia, and Brazil, the diamond is found associated with platinum and gold, which does not appear to be the case with the African specimens, at least as far as the former metal is concerned. J. W.

The Brown-Coal of the Bauerberg, near Bischoffsheim, vor der Rhön. By A. HILGER (*Jahrb. für. Min.*, 1877, 420—421).—A brown-coal deposit occurs in the south-western slope of the Hohen Rhön, in four or five thick strata, separated from each other by a thin layer of a bituminous mixture of iron pyrites, clay, and basaltic tufa. The brown-coal is partly earthy and partly massive or dense, stems of fossil trees, 5 or 6 feet thick, being often found in the strata. The thickness of the individual strata varies from 3 to 16 feet, the total thickness of the deposit being 50 feet. The uppermost stratum consists generally of a dense lignite, then follows earthy brown-coal, the lowermost stratum consisting, however, of lustrous black bituminous coal, and resting upon basalt. A former examination of these brown coals, made by Klinger, proved them to be composed as follows, viz.:—

	Carbon.	Hydrogen.	Oxygen and Nitrogen.	
Lignite	64·22	5·56	23·52	= 93·30
Brown-coal	61·74	4·94	20·60	= 87·28
Bituminous coal	76·43	8·88	13·99	= 99·30

The author determined the amount of ash and water in the above, obtaining the following results:—

	Water.	Ash.
Bituminous coal........	11·6	8·5
Brown-coal	12·4	10·4
Sandy-coal	16·2	77·94
Clayey-coal	14·4	26·10
Lignite................	15·2	9·8

A greyish or yellowish mass is found in the *débris* of the exhausted mines, the greater part of which is found to be *ammonium alum* containing a small quantity of sulphur, ferric oxide, and clay. It is, of course, a product of the completely weathered brown-coal "slack," and of great importance to the alum trade. The author also analysed a granular, crystalline, ochrey-yellow efflorescence, which occurs on the clay-substance interposed between the brown-coal strata, and found it to have the following composition, viz.:—

Al_2O_3.	Fe_2O_3.	Fe_2O.	MgO.	SO_3.	H_2O.	
16·7	4·2	2·9	2·3	39·3	33·3	= 98·7

from which it appears to be keramohalite. It is soluble in water.

C. A. B.

On the Production of Artificial Corundum, Ruby, and different Crystallised Silicates. By E. Frémy and Feil (*Compt. rend.*, lxxxv, 1025—1035).—Synthetical mineralogy or the artificial production of minerals throws, the authors think, the greatest light on the natural production of mineral substances, and enables us to solve certain problems in their composition which analysis leaves to a certain extent undecided, as the purest minerals contain foreign bodies impossible of distinction by analysis, but which their synthetical production eliminates.

A large number of minerals have already been produced in the wet way, and the important results of Becquerel and Hautefeuille show the advantage of this line of research. Corundum is, perhaps, the mineral which has been most investigated by chemists, as the names of Ebelmen, de Senarmont, St. Claire Deville, Caron, Gaudin, and Debrée show. The authors think, therefore, that the methods they have employed for producing crystallised alumina coloured by various pigments will be of interest, and may find an application in the arts; they further add that the methods they employ may be used for the production of other minerals.

Wishing to approach as nearly as possible the natural conditions for the production of corundum, they have used furnaces capable of producing the highest temperature and of maintaining it for a long time; they have also acted on masses of 20 to 30 kilograms. Among other furnaces they have employed a regenerative gas furnace, used in the production of plate-glass.

The method which produced the largest quantity of crystallised alumina was the following:—A fusible aluminate is heated to a bright redness in contact with a silicious substance. The alumina being gradually disengaged from combination, crystallises in presence of a flux. The authors attribute this crystallisation to different causes.

a. The volatilisation of the base united to the alumina.
b. The reduction of this base by the gases of the furnace.
c. The formation of a fusible silicate by the combination of the silica with the base.
d. A phenomenon of liquidation, producing a very fusible silicate and refractory alumina.

All these cases have occurred during the experiments. The authors think that the best method of crystallising alumina is to replace it by silica (*c*). Aluminate of lead, the authors have, up to the present, found to be the one best suited for this purpose.

Equal weights of alumina and minium are heated to a bright redness in a fire-clay crucible; on cooling two products are found, one vitreous, consisting mainly of lead silicate, the other crystalline and containing geodes filled with fine crystals of alumina, the sides of the crucible itself supplying the silica necessary for the reaction; by this method crystals of white corundum are obtained: when rubies are required, 2 to 3 per cent. of potassium bichromate are added to the mixture, and oxide of cobalt gives sapphires. The crystals found in the geodes have the composition, adamantine lustre, hardness, density, and form of natural rubies; they scratch quartz and topaz. Specific gravity 4—4·1, like natural rubies they lose colour on strong ignition, and regain it on cooling. Lapidaries have found them quite as hard as the natural stones. When polarised they show a black cross and coloured rings.

The crystallised silicates shown by the authors at the same time were obtained by means of fluorides, and M. Daubray's observations were fully confirmed that fluorine takes a most important part in the formation of mineral deposits. They have found that in this direction aluminium fluoride is the most active. Equal weights of silica and aluminium fluoride heated to redness for several hours give a crystalline body, probably disthene, and fluoride of silicon. These crystals have the composition $SiO_2 = 47·65, Al_2O_3 = 51·85$, loss $= ·50$, and closely resemble natural disthene. The crystals appear to belong to one of the oblique systems.

The action of aluminium fluoride on boric acid gave a crystallised aluminium borate which corresponds with disthene. The authors are now engaged in a series of experiments on the action of aluminium fluoride on other inorganic acids. When equal weights of alumina and barium fluoride, together with 2 or 3 per cent. of potassium bichromate, are treated at a high temperature for a considerable time in a crucible covered by another so as to form a condenser, two kinds of crystals are obtained; some, which appear to have been volatilised, are long colourless prisms with the appearance of antimony glance; the others are regular crystals of ruby of a fine rose colour. The long prismatic crystals are a double silicate of barium and aluminum, having the composition $SiO_2 = 34·32$, $BaO = 35·04$, $Al_2O_3 = 33·37$. These two substances seem to be the result of the following transformations. The calcination of the mixture, forming aluminium fluoride and baryta, the fluoride of alumina probably acting in two different ways.

(*a.*) Decomposed by the gases of the furnace, it formed hydrofluoric acid and corundum.

(*b.*) By acting on the silica of the crucible, it formed aluminium silicate, which, by its action on the baryta, produced the double silicate above mentioned.

The authors call attention to the fact that these crystals occupy a position in the crucibles pointing to their having undergone volatilisation, and yet it is impossible to alter them when obtained, even at the highest temperatures; this they think is due to the action of fluorides which act as carriers of less volatile substances. In support of this they recall the remarkable crystals of orthose felspar found in the upper part of a copper furnace at Mansfeld, which were due to the fluoride of calcium used as a flux. This action of barium fluoride on alumina in presence of silica is probably one example of a general phenomenon of the decomposition of fluorides by different bases. The authors hope to describe other crystallised double silicates produced under the same conditions as the one above mentioned, and will then give the general formulæ of these compounds. In conclusion the authors say that they have carried out these investigations simply for their scientific interest, and that they therefore publish them without reserve, and will be happy to hear of any application in the arts which may result from them. J. M. T.

Artificial Formation of Albite and Orthose. By P. HAUTEFEUILLE (*Compt. rend.*, lxxxv, 1043—1046).—Felspars the author considers to be a most important group of minerals, as they are the principal constituents of almost all eruptive rocks. Up to the present time it had not been possible to produce them artificially, at least in well-defined crystals; they have, however, been accidentally produced in copper furnaces both at Mansfeld and in the Hartz. These the author thinks must have been formed by sublimation with the aid of the calcium fluoride employed as flux. As orthose is fusible, attempts have been made to crystallise it by slow cooling, but without success. M. Hautefeuille, having prepared successfully the principal minerals of titanium, has also succeeded in obtaining orthose and albite, and hopes soon to prepare the other species of the same group.

His process consists in heating the elements of these minerals in presence of certain fused salts, such as tungstic acid or alkaline tungstates: thus a mixture of silica and alumina in presence of acid potassium tungstate, at a temperature between 900 and 1,000°, produces tridymite, orthose, and triclinic felspars. If the potash and alumina are in the proper proportions, the tridymite and triclinic felspars disappear after 15 to 20 days' heating, and the orthose alone remains. A highly alkaline silicoaluminate of potash containing one of Al_2O_3 to six SiO_2 mixed with tungstic acid gives the same result. When soda is substituted for potash, other conditions remaining the same, albite is formed. The analyses of these products give the proportions of oxygen contained in the alkali (K or Na), in the alumina and in the silica as 1 : 3 : 12, these being the proportions characterising orthose, microcline, and albite. Like the natural ones, the crystals artificially obtained are not attacked by acids; their sp. gr. respectively being 2·61 and 2·55. The crystallographic examination of the artificial albite shows that it almost exactly resembles the natural crystals from Dauphiné and the Tyrol. The crystals having the composition of orthose appear to be analogous to those described by Mr. Mallard found in the St. Gothard. The author thinks that the orthose and albite having been obtained under exactly the same conditions, the pseudomorphism of this group of silicates is simply due to the nature of the alkali. While showing the interest attached to the preparation of these minerals in the dry way, he in no wise wishes to deny that the wet way may have often been employed by nature in the formation of the same species. J. M. T.

Chemical Constitution of Hatchettolite and Samarskite from Mitchell County, North Carolina. By OSCAR D. ALLEN (*Amer. J. of Sci.* [3], xiv, 128—131).—I. *Hatchettolite.*—In March, 1876, Dana described a mineral which was associated with the samarskite of Mitchell county, and in May, 1877, Lawrence Smith published an analysis of this mineral for which he proposed the name of hatchettolite. The specimen obtained by the author was from the same source, and consisted of a large but imperfect crystal, of which about 12 grams appeared sufficiently pure for analysis. Pieces from different parts of the mass gave the specific gravities 4·77, 4·84, 4·82, 4·990, 4·76; the mineral described by Dana had a specific gravity of 4·794.

The results of two analyses by the author are given in the first two columns; the third column contains the numbers given by Lawrence Smith.

	Ta_2O_5.	Cb_2O_5.	TiO_2.	WO_3 u. SnO_2.	U-oxide.	CaO.	Yttria and Cerium oxides.
I. ..	29·83	34·240	1·61	0·30	15·50	8·87	—
II. ..	29·60	35·96	—	—	—	8·89	—
III..	67·86		—	0·60	15·63	7·09	0·86

	FeO.	MgO.	K_2O and Na_2O.	Water easily heated.	
I.	2·19	0·15	1·37	4·49	= 98·55
II.	2·33	—	—	—	
III.........	2·51	—	1·21	4·42	= 100·18

I and II also contained a trace of lead.

The separation of tantalic and columbic acids was effected by Marignac's method. The composition of the mineral may be represented by the formula $R^{ii}_2R^{v}_2O_7 + 2R^{ii}R^{v}_2O_6 + 4H_2O$, where R^{ii} represents one atom of a bivalent basic radicle or two of sodium, and R^{v} represents Ta or Cb. Hatchettolite may have resulted from alteration of a mineral having essentially the same chemical constitution, as well as crystalline form, as pyrochlore, an alteration consisting of hydration and removal of alkaline fluorides.

II. *Samarskite.*—The analysis of this mineral gave results as follows:—

	Cb_2O_5.	Ta_2O_5.	SnO_2.	Y_2O_3.	Uranium oxides.	Cerium oxide.
I.	37·81	17·79	—	14·52	4·10	12·63
II.....	37·20	18·60	0·08	14·45	4·24	12·46

	MnO.	FeO.	CaO.	H_2O.	
I.	0·80	10·60	—	—	
II.	0·75	10·90	0·55	1·22	= 100·45

These results do not differ materially from the first published analysis of samarskite from the same locality by Miss E. H. Swallow. They agree sufficiently well with the formula $R^{ii}_2R^v_2O_7 + R^{ii}R^v_2O^s$.

F. D. B.

Occurrence of Tinstone at Truro. By Crozet (*Chem. Centr.*, 1877, 120).—A valuable deposit of tinstone is situated under the water of the small drift of Restronguet, near Truro. It is covered with mud and sand. After working this ore at various periods, it was given up in 1843. In 1871, however, the working was again commenced. The ground was examined by boring in the open sea, and it was found that the deposits, which rested immediately on the rocky bottom, had a thickness of 0·45 to 1·20 meters, and were covered with mud and sand to a depth of 18 meters. The richest portions of the ore formed pure crystals of stannic oxide (*Bull. Soc. de l'ind. minér; B. u. Hüttenm-Z.*, xxx, 443). D. B.

Galenite from Habach in Salzburg. By V. von Zepharovich (*Jahrb. f. Min.*, 1877, 529).—The galenite from this locality is remarkable, firstly, for its very complete octohedral cleavage, with a less complete cubical cleavage; and secondly, through the occurrence of numerous interpolated twin lamellæ parallel to a face of 3O3. The unusual cleavage mentioned above has been observed before only in the case of galenite from Pennsylvania. There was no appreciable difference in the lustre of the two kinds of cleavage-surfaces. The behaviour of this galenite, on being heated in a mattrass, is striking, as it does not decrepitate; whilst the heated portions have a ready cubical and only an indistinct octohedral cleavage. Sp. gr., 7·50; chem. com. = 98·03 per cent. of lead sulphide and 1·97 per cent. of bismuth sulphide. The interpolated twin lamellæ are generally so thin that they are scarcely discernible with the naked eye, and are observed also on the respective cleavage-faces of the large crystal exhibiting identical cleavage faces. C. A. B.

An Aragonite Crystal from Oberstein on the Nahe. By H. Laspeyres (*Jahrb. f. Min.*, 1877, 527).—Calcite is often found in amygdaloïdal cavities in melaphyr, but aragonite was unknown to it until the author discovered it in the above-mentioned locality. The crystal in question has a length of 13 c.m., and a thickness of 4·5 c.m. It is a penetration quadraling, the twin plane being a face of ∞P, and the combination is $\infty P . \infty P\breve{\infty} . \frac{1}{2}P . P\breve{\infty} . 0P$; the latter face is not striated in the direction of the brachydiagonal. C. A. B.

A Polysynthetical Augite-twin from Bell, near Laach. By H. Laspeyres (*Jahrb. f. Min.*, 1877, 527, 528).—A polysynthetical twin-development in the monosymmetrical system is of rare occurrence. It is most common with epidote, and more rare with orthoclase and augite. G. vom Rath (*Jahrb. f. Min.*, 1876, 404) described a crystal of fassaite from Traversella, which consisted of one large individual, with two interpolated twin-plates of the same substance. The author observed an augite-twin from Bell, exhibiting the usual forms, with a twin-plate (interpolated parallel to the orthopinacoid), having half the thickness of the two halves of the principal individual. C. A. B.

Analysis of a Trachyte from Wolferdingen, in the Westerwald. By A. Hilger (*Jahrb. f. Min.*, 1877, 421, 422).—The specific gravity of this specimen was found to be 2·68, and its chemical composition as follows, viz.:—

SiO_2.	Al_2O_3.	Fe_2O.	FeO.	MnO.	CaO.	MgO.
59·87	22·52	0·32	2·52	0·13	2·5	0·46

K_2O.	Na_2O.	P_2O_5.	H_2O.
4·42	5·78	0·3	2·24 = 101·06.

with traces of Cl, SO_4H_2, Li, Ba, and Sr. Before this the presence of these bodies had rarely been proved, von Lasaulx describing a trachyte from Mont Dore, which contained Li and Ba. C. A. B.

The Primary Rocks of the Northern Schwarzwald. By C. Hebenstreit (*Jahrb. f. Min.*, 417—419).—The author undertook the task of ascertaining the composition of the basic and acid rocks of the wide-spread gneiss district of the Kinzigthal. Three varieties of these rocks were examined, viz.: (1.) A granular gneiss, rich in silica and poor in mica; (2.) A hornblendic rock, enclosed in the gneiss; (3.) A garnet-graphite-gneiss, rich in mica. Garnet-gneiss was known to occur often in the Schwarzwald; but garnet-graphite-gneiss was hitherto unknown, the latter being formerly known by the name of Kinzigite. This rock is found at Schenkenzell, near Wittichen, in a layer scarcely 1½ feet in thickness, enclosed in ordinary gneiss. It is coarsely laminated, macroscopically distinctly striated plagioclase; black mica, violet-red garnet, and laminæ of graphite are recognisable. Colourless needles of apatite, fine aggregates of iron-pyrites and reddish specks of specular-iron were detected in the felspar, on examining the rock under the microscope. The presence of quartz could not be detected. Its specific gravity was found to be 3·00. An analysis made of a pure, fresh specimen furnished the following results, viz.:—

(1.) By experiment; (2.) Calculated from No. 1, after deducting iron-pyrites, apatite, graphite, and iron-glance.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.
No. 1 ..	44·53	17·55	3·38	12·60	3·36	5·68	3·54
No. 2 ..	46·68	18·40	3·54	12·87	3·32	5·95	3·72

	Na_2O.	H_2O.	P.	S.	Graphite.	
No. 1	3·60	1·66	0·17	0·29	4·33	= 100·69
No. 2	3·77	1·75	—	—	—	= 100·00

The author also examined the asymmetrical felspar and garnet observed in the rocks, and found the former to be colourless strongly lustrous oligoclase, with a specific gravity of 2·657, and exhibiting a fine twin striation; whilst the latter was true almandine, containing many enclosures (particularly microlitic quartz), and had a specific gravity of 3·96. The analyses of these minerals furnished the following results, viz.:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	
Oligoclase	62·90	22·23	trace	—	4·45	—	2 09	8·48	= 100·15
Garnet	37·40	21·08	2·01	28·49	3·05	8·22	—	—	= 100·25

Hebenstreit gives a table of analyses of gneissoïd rocks, comparing them at the same time with analyses of rocks from the same neighbourhood, the result of which serves to show that the hornblendic rocks and the garnet-gneiss (which is intimately associated with the hornblendic rocks) have been separated from the very common and widely-spread granular striated gneiss, and are equally basic in character. The granular gneiss is the most acid of these rocks. An examination of the granite of Tryberg proved it to resemble very closely the granites from the northern Schwarzwald. The composition of the gneiss from the neighbourhood of Tryberg was found to differ considerably from that of the granite from the northern Schwarzwald.

C. A. B.

Analysis of the Water of the Warm Spring at Assmannshausen. By R. FRESENIUS (*J. pr. Chem.* [2], xvi, 278—290).—This water was found to contain in 100,000 parts (salts all anhydrous):—

Na_2CO_3.	Li_2CO_3.	$CaCO_3$.	$BaCO_3$.	$SrCO_3$.	$MgCO_3$.
9·7486	1·7460	12·2307	0·0989	0·1978	4·0066

$FeCO_3$.	$MnCO_3$.	K_2SO_4.
0·2239	0·1326	4·3068

KCl.	NaCl.	NaBr.	NaI.	Na_2HPO_4.	SiO_2.	CO_2 (combined).	CO_2 (free).
0·4522	57·1764	0·0571	0·0004	0·0301	3·1539	12·7780	18·5800

The sp. gr. of the water was 1·000832 at 15°, and its temperature 31·1° C. The water is distinguished from all others of similar character by the relatively large quantity of lithium which it contains.

J. R.

Analysis of the Acid Well (Sauerbrunnen) at Bilin. By HUPPERT (*Chem. Centr.*, 1877, 137).—This is a newly-discovered spring, and the analysis of one of the older springs, the Josefsquelle, is added for comparison.

	Josefsquelle.	New spring.
K_2SO_4	2·3496	2·5418
Na_2SO_4	7·2762	7·0767
NaCl	3·8135	3·7191
Na_2CO_3	33·3085	32·6576
$CaCO_3$	4·1295	4·2825
$MgCO_3$	1·7191	1·8954
Li_2CO_3	0·1133	0·1253
$FeCO_3$	0·0284	0·0259
$MnCO_3$	0·0305	0·0105
Iodine	trace	trace
$Al_2O_3.P_2O_5$	0·0057	0·0056
SiO_2	0·4340	0·4357
Total solids	53·2088	52·7761
Half-combined CO_2	16·7303	16·5087
Free CO_2	14·2697	15·3316
Total of constituents	84·2083	84·6164
Total CO_2	47·5565	48·3480

G. T. A.

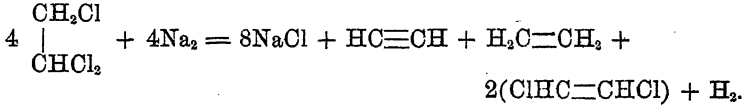
Organic Chemistry.

Decomposition of Organic Liquids by the Electric Spark, with production of the Fundamental Hydrocarbons. By P. TRUCHOT (*Compt. rend.*, lxxxiv, 714—716).—According to Berthelot, when a hydrocarbon of high molecular weight is submitted to destructive distillation, the four fundamental hydrocarbons, acetylene, ethene, methane, and ethane are first separated, and these, immediately entering into combination with each other, produce the more complex hydrocarbons which are actually obtained. It is obvious that this assumption would be greatly strengthened if the decomposition could be effected in such a manner that, recombination being prevented, the simpler hydrocarbons were obtained in the free state. This the author has succeeded in doing by passing a powerful induction spark through the liquid itself, and collecting the resulting gases.

Volatile liquids, such as pentane, pentene, and ethyl oxide give about one litre of gas per hour, but compounds of higher boiling point give considerably less. The gas invariably contained hydrogen in addition to the hydrocarbons already mentioned, but no compound containing more than two atoms of carbon in the molecule was present. With the liquid paraffins, no deposit of carbon occurred during the decomposition, provided the liquid was kept slightly warm; and a trace of carbon only was obtained in the case of an olefine. With the less saturated hydrocarbons, however, such as the turpentines and benzene-derivatives, a tolerably abundant deposit of carbon always resulted. Compounds containing oxygen, such as alcohol, ether, and the aldehydes give no carbon; but, in addition to the fundamental hydrocarbons, evolve carbon monoxide, unaccompanied by carbon dioxide or water-vapour. J. W.

Action of Aluminium Iodide on various Organic Compounds containing Chlorine. By G. GUSTAVSON (*Chem. Centr.*, 1877, 19).—Aluminium iodide has no action even with the aid of heat on C_6Cl_6 and C_2Cl,(C_2Cl_4(?)). It acts easily on C_2Cl_6 according to the equation $3C_2Cl_6 + Al_2I_6 = 3Cl_2Cl_4 + Al_2Cl_6 + 3I_2$. But there is also formed an amorphous carbon compound containing iodine. Aluminium iodide acts energetically on trichlorhydrin, yielding iodine, allyl iodide, and aluminium chloride. In the benzene series the chlorine of the lateral chains only is replaced by iodine, when they are acted on by aluminium iodide. G. T. A.

Action of Sodium upon Monochlorethylene Chloride. By H. BRUNNER and RUD. BRANDENBURG (*Deut. Chem. Ges. Ber.*, x, 1496—1499).—The authors have demonstrated that monochlorethylene chloride is decomposed by sodium into acetylene, ethylene, and ethylene dichloride, according to the equation—



$$4\begin{array}{l}CH_2Cl\\ |\\ CHCl_2\end{array} + 4Na_2 = 8NaCl + HC\equiv CH + H_2C=CH_2 + 2(ClHC=CHCl) + H_2.$$

This is in keeping with the observation of Fuchs on the decomposition of vinyl bromide by sodium into acetylene and ethylene, and affords a sufficient explanation of the failure of the author's attempts to introduce the vinyl molecule into the benzene nucleus by means of the action of sodium upon a mixture of chlorethylene chloride and benzene bromide. C. F. C.

The Preparation of Propyl Glycol. By O. HARTMANN (*J. pr. Chem.* [2], xvi, 383).—The author obtained 5 grams of propyl glycol from 125 grams of propylene bromide (b. p. 141°) by Zeller and Hüfner's reaction. Hence Voelker's statement (*Deut. Chem. Ges. Ber.*, ix, 924) that potassium carbonate has no action on propylene bromide is incorrect. W. C. W.

Compounds of Quercite with Butyric and Acetic Acids. By L. PRUNIER (*Compt. rend.*, lxxxiv, 1318).—The compounds of quercite with stearic, benzoic, and tartaric acids have been described by Berthelot. The author describes the following compounds of quercite with butyric acid:—

$$\underset{\text{Monobutyrin.}}{C_6H_{10}O_4(C_4H_8O_2)} = \underset{\text{Quercite.}}{C_6H_{12}O_5} + \underset{\text{Butyric acid.}}{C_4H_8O_2} - H_2O.$$

$$\underset{\text{Tributyrin.}}{C_6H_6O_2(C_4H_8O_2)_3} = C_6H_{12}O_5 + 3C_4H_8O_2 - 3H_2O.$$

$$C_6H_2(C_4H_8O_2)_5 = C_6H_{12}O_5 + 5C_4H_8O_2 - 5H_2O.$$

Pentabutyrin.

The three corresponding acetins are also described.

The *monobutyrin* is produced when 1 part of quercite is heated with 3—4 parts of butyric acid to 110—120° for twelve hours in sealed tubes. It is mixed with some higher compounds, and with a large quantity of uncombined quercite.

The *tributyrin* is produced when the mixture is heated to 150—160°.

The *pentabutyrin* is produced at 170—180°.

All these ethers are solid or viscid bodies, amorphous, colourless, and slightly deliquescent, of bitter taste; very soluble in ether, less so in alcohol, and very slightly in water, unless this latter contains an excess of butyric acid, in which case the ethers dissolve, and by cautious addition of water the pentabutyrin and tributyrin are separated as an emulsion, the former being precipitated, and the latter rising to the top.

The method of separation of these bodies is precisely the same as that used by Berthelot in the separation of the acetins, butyrins, &c., of glycerin, except that potash must be added to slight alkaline reaction, so as to remove the free acid which these bodies dissolve and retain obstinately.

The following are the analytical results, which were in each case controlled by titration with baryta-water:—

	Monobutyrin.		Tributyrin.		Pentabutyrin.	
	Found.	Calc. for $C_6H_{10}O_4(C_4H_8O_2)$.	Found.	Calc. for $C_6H_6O_2(C_4H_8O_2)_3$.	Found.	Calc. for $C_6H_4(C_2H_3O_2)_5$.
C..	51·3	51·1	57·9	57·70	60·1	60·70
H.	7·8	7·6	8·2	8·02	8·3	8·15

The first two contained small quantities of higher compounds.

Acetins.—Crystallisable acetic acid heated to 100—120° with quercite combines with it slowly to form the monoacetin. If a small quantity (about ·01) of acetic anhydride be added, and the mixture heated to 130—140°, the triacetin is formed. The pentacetin is formed when quercite is heated with acetic anhydride. The method of purification is the same as with the butyrins.

The acetins of quercite resemble the butyrins; they are amorphous, colourless, solid and brittle, or viscid bodies, of bitter taste and somewhat agreeable odour.

The following are the analytical results:—

	Pentacetin, $C_6H_2(C_2H_4O_2)_5$.		Triacetin, $C_6H_6O_2(C_2H_4O_2)_3$.	
	Found.	Calculated.	Found.	Calculated.
C ...	51·15	51·30	49·3	49·65
H ...	6·10	6·00	6·4	6·20

C. W. W.

Substituted Crotonic Acids from the Pyrocitric Acids. By T. MORAWSKI (*Chem. Centr.*, 1877, 131—133).—The author pointed out in a paper on mesaconic acid (*Chem. Centr.*, 1876, 262—294), that the monobromocrotonic acid which is formed from mesaconic acid by means of the intermediate mesadibromopyrotartaric acid, is converted by the action of sodium amalgam into isobutyric acid, as is the case on similar treatment with Kekulé's monobromocrotonic acid from citraconic acid. The supposition that the two acids are identical has been confirmed by the author by a comparison of their salts. The first salts formed with the monobromocrotonic acids derived from citraconic and mesaconic acids were the calcium and copper salts.

The *calcium salt* of both acids is moderately soluble in water, and crystallises on evaporation of the solutions. It is stable in air, and loses its water of crystallisation quickly and perfectly at 100°, but only slowly in a vacuum over sulphuric acid. The *copper salt* is in each case of a bright blue colour; becomes lighter on drying, and has the composition of a basic salt. The *cadmium salt* of each acid crystallises in brilliant prisms, and appears to be hydrated. The crystals, dried at 100°, were of a faint yellow at the edges, and the amount of cadmium corresponded with the anhydrous salt. With the monobromocrotonic acid derived from citraconic acid a *barium salt* was obtained which was easily soluble in water, and separated from concentrated solutions in prismatic crystals. An ammonium salt was also prepared from the same acid, which crystallised easily, and seemed to be volatile in a vacuum over sulphuric acid. The soluble salts of the acids from both sources gave with ferric chloride bright flesh-coloured precipitates.

The author next examined the monochlorocrotonic acid which Gottlieb obtained by means of zinc from trichlorobutyric acid, and that which Swarts obtained by decomposition of citradichloropyrotartaric acid with bases, and found them to be identical. The following salts were prepared from Gottlieb's acid. The *calcium salt*, when it separates from a cold solution on slow evaporation, forms light, loose, efflorescent crystals, which overtop the side of the vessel; but when deposited from a hot concentrated solution, it crystallises in distinct needles, which adhere to the sides of the vessel, giving them a fine silky lustre. The *copper salt* is a bright blue powder, which dissolves with great difficulty in water. It is a basic salt, and consists of $(C_4H_4ClO_2)_2Cu + Cu(OH)_2$. The *sodium salt* is easily soluble in water, but not without difficulty in alcohol. It crystallises imperfectly, and seems to be hydrated. It gives a bright flesh-coloured precipitate with ferric chloride. The *ethyl-compound* of monochlorocrotonic acid is a mobile liquid, obtained by treating an alcoholic solution of the acid with hydrochloric acid gas, washing with water and caustic soda, and drying over calcium chloride. The ether is sparingly soluble in water, has a pleasant fruity smell, can be distilled without change, and boils at 155—158°.

A few salts were also prepared from dichlorocrotonic acid, obtained from trichlorobutyric acid by the action of alkalis. The *potassium salt* crystallises in very fine large rhombohedrons. The *copper salt* has an intensely green colour. It is less soluble in hot than in cold water, so that if a solution saturated at ordinary temperatures is raised to boiling it becomes turbid, and at last is filled with the separated green salt. The *ammonium salt* dissolves with extraordinary ease in water. A crystalline mass was obtained by evaporating the solution over sulphuric acid, which was neutral and anhydrous. It gives a light flesh-coloured precipitate with ferric chloride. The *barium salt* is very easily soluble in water, but crystallises with difficulty. An alcoholic solution deposits very small crystals on the side of the vessel, which, however, appear to be very deliquescent. G. T. A.

Action of Chlorocarbonic Ether on Sodium Cyanamide. By Paul Bässler (*J. pr. Chem.* [2], xvi, 125—169).—When chlorocarbonic ether is gradually added to dry sodium cyanamide suspended in anhydrous ether, a reaction begins which at first requires moderating by cooling, but which must be completed on the water-bath. The filtrate, after evaporation of the ether, forms a thick, very sour syrup, containing much cyanamidocarbonic ether. On being heated to over 140° it yields a new body, cyanamidodicarbonic ether, together with cyanamide and its polymerisation product, *dicyanodiamide*.

Cyanamidodicarbonic ether, $C_7H_{10}N_2O_4 = N(CN)(COOC_2H_3)_2$, consists of very large glittering crystals, which melt at 32·8° to an oily liquid, resolidifying only at a much lower temperature. It is readily soluble in alcohol, ether, chloroform, and benzene, less soluble in carbon bisulphide and sulphuric acid, but insoluble in water. On dry distillation it yields carbon dioxide and cyanic ether, together with the decomposition products of the latter. Water gradually resolves it into carbon dioxide, alcohol, and cyanamidocarbonic ether, which last is in turn split up into carbon dioxide, alcohol, and cyanamide. With ammonia it yields cyanamidocarbonic ether and ethyl carbamate. Heated to 150° with sodium ethylate in sealed tubes it yields ether, sodium, ethylcarbonate, and the sodium salt of cyanamidocarbonic ether.

Cyanamidocarbonic ether, $C_4H_6N_2O_2 = N(CN)(COOC_2H_5)H$, is prepared by the action of concentrated sulphuric acid on sodium cyanamidocarbonic ether. When pure it is an oily thick syrup, of a yellow colour, and with a strong sour reaction and burning taste. It has an ethereal odour. It is soluble in alcohol, ether, chloroform, and benzene, less soluble in carbon disulphide, and somewhat soluble in water. Boiling water converts it into carbon dioxide, alcohol, and cyanamide, and boiling dilute hydrochloric acid into ethyl allophanate. On being heated it yields cyanamide and cyanamidodicarbonic ether. Cyanamidocarbonic ether readily forms stable salts, which are generally characterised by forming magnificent crystals with a peculiar satiny lustre.

Sodium-cyanamidocarbonic ether, $N(CN)(COOC_3H_5)Na$, crystallises in splendid glittering crystals, melting at 241°, and soluble with great ease in water, less soluble in hot absolute alcohol, and still less in cold alcohol. On heating it splits up into a mixture of ethyl and sodium cyanates.

Potassium-cyanamidocarbonic ether, $N(CN)(COOC_2H_5)K$, is formed when cyanamidodicarbonic ether is treated with alcoholic potassium hydrate. It crystallises in magnificent white glittering needles of very voluminous character. They melt at 199°, and are readily soluble in water, slightly soluble in absolute alcohol in the cold, but more easily on warming.

Silver-cyanamidocarbonic ether, $N(CN)(COOC_2H_5)Ag$, is obtained as a curdy white precipitate by adding either of the previous compounds to a solution of silver nitrate. It is easily soluble in ammonia and dilute nitric acid.

Ethyl-cyanamidocarbonic ether, $N(CN)(COOC_2H_5).C_2H_5$, is formed by heating in sealed tubes to 150° a mixture of ethyl iodide and potassium cyanamidocarbonic ether. It is a colourless, neutral, oily liquid, boiling at about 213°, and miscible in all proportions with alcohol and ether. It is slightly soluble in cold water, but rather more soluble in hot water. It can be inflamed with difficulty, and burns with a violet-red flame. This new body is isomeric with dicyanic ether and a polymeride of ethyl cyanate. E. N.

Action of Thiocyanic Acid on Alcohols. By E. BLANKENHORN (*J. pr. Chem.*, [2], xvi, 358—383).—Ethylic dithioallophanate, $C_4H_8N_2S_2O$, was obtained by Lössner (*J. pr. Chem.*, [2], vii, 474), by the action of phosphorous chloride on an alcoholic solution of potassium thiocyanate, and was considered by him to be $C_8H_{16}N_4S_4O$. It is best prepared by adding fuming hydrochloric acid to a hot concentrated alcoholic solution of potassium thiocyanate; potassium chloride separates out, and the filtrate, after concentration, deposits crystals of ethylic dithioallophanate. An excess of hydrochloric acid must be avoided, as its presence is favourable to the production of thiourethanes.

Ethylic dithioallophanate floats on the surface of cold water without dissolving; it is soluble in boiling water, in boiling ether, and in alcohol. The alcoholic solution deposits regular prismatic crystals, melting with decomposition at 170—175°, and having a bitter taste. It is decomposed by the action of alcoholic ammonia at the ordinary temperature, into urea, mercaptan, and thiocarbamide, but when heated to 150°, in sealed tubes, it forms thiocarbamide and ethyl alcohol. Aniline converts it into thiocarbamide, diphenylcarbamide, and mercaptan, and baryta or alcoholic potash decomposes it, forming mercaptan, thiocarbamide, and carbon dioxide. From these reactions it follows that the probable constitution of ethylic dithioallophanate may be represented by the formula, $NH_2—CS—NH—CO—SC_2H_5$. The author has not yet succeeded in preparing methyl- and butylthioallophanates.

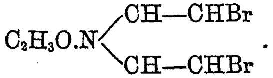
A mixture of two isomeric *thiourethanes* is obtained by acting on alcoholic solutions of potassium thiocyanate, with an excess of strong hydrochloric acid, *e.g.*, *xanthamide* and *carbonylthioethylamine*, described by Conrad and Salomon (*J. pr. Chem.*, [2], x, 28), are obtained by adding hydrochloric acid to a solution of potassium thiocyanate in ethyl alcohol. By substituting methyl for ethyl alcohol, a mixture of methylxanthamide, $NH_2—CS—OCH_3$, and carbonylthiomethylamine, $NH_2—CO—SCH_3$, is produced. The last-mentioned substance is deposited from its alcoholic solution in large, monoclinic prisms, which melt at 95—98°.

A mixture of isobutylxanthamide, $NH_2—CS—OC_4H_9$, and carbonylmonothioisobutylamine, $NH_2—CO—SC_2H_3(CH_3)_2$, is formed by the action of an aqueous solution of potassium thiocyanate on isobutyl alcohol which has been saturated with hydrochloric acid gas.

W. C. W.

On the Constitution of Pyrrol. By ROBERT SCHIFF (*Deut. Chem. Ges. Ber.*, x, 1500—1503).—By the action of acetyl anhydride upon pyrrol (b. p. 133°), the author obtains an *acetyl pyrrol* (m. p. 90°). Finding that both ethyl iodide and the alkali metals, in presence of anhydrous ether, fail to exert any action upon this compound, and that therefore there is no second atom of hydrogen in union with the nitrogen, he appears to have established the presence of the NH group in pyrrol.

By the action of bromine on this compound, a *bibromacetylpyrrol* is formed, to which the author assigns the constitution:—



The preparation and investigation of the derivatives of this body are in progress.

C. F. C.

Peculiar Formation of Phenyl Isocyanide. By C. O. CECH and P. SCHWEBEL (*Chem. Centr.*, 1877, 134).—When dichloracetic acid is brought into contact with aniline, the mixture solidifies, with strong evolution of heat. This solid, recrystallised from alcohol, yields yellowish, brilliant needles, which melt at 125°, and consist of aniline dichloracetate. On treatment of this body with dilute caustic soda, no aniline is liberated, but on boiling the liquid, phenylisocyanide is formed, together with formic and hydrochloric acids.

G. T. A.

Cyanoguanidines. By OSCAR LANGREBE (*Deut. Chem. Ges. Ber.*, x, 1587—1596).—Hofmann has shown that aniline, toluidine, and cumidine form addition-products with cyanogen, and that melaniline (diphenylguanidine) also possesses the same property; the author has examined the action of cyanogen on ditolylguanidine; combination readily takes place when cyanogen is passed through a cooled ethereal solution of the base, a magma of crystals being formed after recrystallisation from warm alcohol (a temperature of upwards of 50° produces decomposition). These have the composition of *dicyanoditolylguanidine*, $C_{17}H_{17}N_5$. This body is very difficultly soluble in water, more readily in ether; at about 70—80° it begins to decompose; by the action of dilute acids it gives rise to *ditolyloxalylguanidine*, $C_{17}H_{15}NO_2$, melting at 188·5°, the reaction being—

$$C_{17}H_{17}N_5 + 2H_2O = C_{17}H_{15}N_3O_2 + 2NH_3.$$

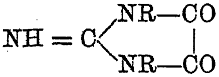
This body is nearly insoluble in water, difficultly soluble in ether and cold alcohol, readily in hot alcohol. Boiling with hydrochloric acid converts dicyanoditolylguanidine into *ditolylparabanic acid*, $C_{17}H_{14}N_2O_3$, by the parallel reaction—

$$C_{17}H_{17}N_5 + 3H_2O = C_{17}H_{14}N_2O_3 + 3NH_3.$$

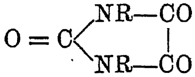
This substance melts at 144°, and is readily soluble in alcohol and benzene, less easily in ether, carbon disulphide, and glacial acetic acid, and almost insoluble in water. In all these reactions the tolylguanidine derivative behaves in a fashion precisely parallel to that exhibited by melaniline; similarly when subjected to the long-continued action of boiling concentrated acids, it forms toluidine, oxalic acid, and carbon dioxide. Alcoholic ammonia at the ordinary temperature did not form an oxaluric derivative, but gave rise to *ditolyl-urea*, $C_{15}H_{16}N_2O$ (melting at 250—260°), and oxalic acid.

To these and analogous bodies the author attributes the formulæ—

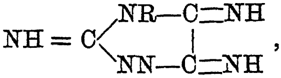
Substituted oxalyl guanidines.



Substituted parabanic acids.



Cyanogen combination products.



it being assumed that ditolylguanidine and similar bodies are $NH = C\{N(C_7H_7)H\}_2$.

By heating ditolyloxalylguanidine with aniline, a phenylated derivative is formed, of basic characters, forming a hydrochloride, $C_{23}H_{19}N_3O_2,HCl$; on similarly heating dicyanodiphenylguanidine and aniline hydrochloride, the hydrochloride of *dicyantriphenylguanidine* is formed, indicated by the formula, $C_{21}H_{17}N_5,HCl,3H_2O$, after crystallisation from hot alcohol. The free base crystallises in needles, containing $C_{21}H_{17}N_5,\frac{1}{2}H_2O$, melting at 172·5° when anhydrous; it is insoluble in water, soluble in alcohol, ether, benzene, and carbon disulphide: with hydrochloric, sulphuric, nitric, and acetic acids it forms well crystallised salts; the platinochloride also is crystalline. This base is not identical with the isomeride which Hofmann prepared by passing cyanogen into α-triphenylguanidine, for Hofmann's product gave no hydrochloride, and formed by the action of dilute acids a yellow triphenyloxalylguanidine, whilst the author's substance does not thus break up, save on long-continued boiling with concentrated acids, when diphenylparabanic acid is formed with difficulty. Hofmann's product readily formed diphenylparabanic acid on boiling with acids. On the other hand, Hofmann obtained a dicyantriphenylguanidine as a bye-product, with preparation of cyaniline, by acting on aniline with cyanogen, which is apparently identical in all respects with the author's product (*Deut. Chem. Ges. Ber.*, iii, 764). The author hence proposes to name the product from α-triphenylguanidine, *α-dicyantriphenylguanidine*, whilst the other isomeride from aniline hydrochloride and dicyandiphenylguanidine (or from cyanogen and aniline) is distinguished as *β-dicyantriphenylguanidine.*

Aniline hydrochloride produces similar bodies with dicyanditolylguanidine, and diphenyloxalylguanidine. These are now under investigation.

C. R. A. W.

Action of Carbonic Oxide on Aniline, Toluidine, Acetylene, &c. By GARNITSCH-GARNITZKY (*Chem. Centr.*, 1877, 22).—Carbonic oxide dissolved in an ammoniacal solution of cuprous chloride, forms with the above bodies tolerably stable crystalline compounds, which probably belong to the ammonia type, and contain the copper in the same condition as the iron in the ferro- and ferricyanides. Ammoniacal solutions of cuprous chloride, free from carbonic oxide, also form crystalline compounds, with considerable evolution of heat; but they are unstable, and rapidly undergo oxidation in the air, which shows that they belong to the suboxide type. G. T. A.

Mono- and Dimethyltoluidine. By A. L. THOMSEN (*Deut. Chem. Ges. Ber.*, x, 1582—1587).—Methyl chloride was prepared by passing hydrochloric acid into pure methylic alcohol containing zinc chloride; the evolved vapours were passed successively through caustic soda, water, and sulphuric acid, and finally into 350 grams of pure fused toluidine, contained in a cohobator, through which steam was passed, so that the toluidine was kept fluid, but yet was condensed and prevented from escaping. After 2½ hours methyl chloride vapours were copiously evolved, showing the methylation to be nearly ended. On shaking with ether, 181 grams of pure toluidine hydrochloride were left undissolved, whilst on agitating the ethereal solution with dilute sulphuric acid, 126 grams of toluidine sulphate were formed, so that little more than one-third of the toluidine had been methylated. The ethereal solution thus deprived of toluidine was evaporated, and the oily base left was treated with acetic anhydride, whereby much heat was evolved, and much *acetomethyltoluidine* produced. From this methyltoluidine was easily prepared by boiling with concentrated hydrochloric acid, and precipitating with soda. From the quantities of toluidine hydrochloride and acetomethyltoluidine obtained, the author calculates that about 2 parts of dimethyltoluidine were formed for every 7 of monomethyltoluidine: but he does not describe the mode of separation of the former body, or even distinctly state that its formation was directly observed.

Acetomethyltoluidine, $C_7H_7.N(CH_3)(C_2H_3O)$, crystallises from a mixture of alcohol and ether in large plates, which fuse at 83°, and boil at 283°; the methyltoluidine thence prepared boils at 208°. On dissolving this in hydrochloric acid, and adding potassium nitrite, with careful cooling, *nitrosomethyltoluidine*, $C_7H_7.N(CH_3)(NO)$, is formed, crystallising from a mixture of alcohol and ether in well defined prisms, melting at 54°. By nitration, methyltoludine forms a dinitro-derivative, crystallising in fine light red needles, melting at 129°, and unaltered by solution in hot acetic or hydrochloric acid.

By treating paratoluidine with methyl iodide, *trimethylparatolylammonium iodide*, $N(CH_3)_3(C_7H_7)I$, is readily obtained, from which *dimethyltoluidine* can be formed by treatment with silver hydrate, and distilling the ammonium hydrate thus produced; it boils at 208° (A. W. Hofmann found 210° for the dimethyltoluidine similarly prepared from paratoluidine). In order to compare this with dimethylorthotoluidine, this body was prepared in a similar fashion from pure orthotoluidine (the aceto-derivative of which melted at 107°); the *dimethylorthotoluidine* thus obtained boiled at 183°. A. W. Hofmann obtained a dimethyltoluidine boiling at 186°, by the action of heat on trimethylphenylammonium iodide, and states in a footnote that he regards this as identical with the ortho-derivative just described, attributing the slight difference in boiling point to thermometric errors; at the same time a dimethyltoluidine, boiling at 205°, was formed; query the corresponding meta-derivative? (*Vide Deut. Chem. Ches. Ber.*, v, 711.)

C. R. A. W.

Diazobenzene-derivatives. By P. G. W. TYPKE (*Deut. Chem. Ges. Ber.*, x, 1576—1582).—Baeyer and Jäger have shown that when aqueous solutions of resorcin and azobenzene are mixed, a red solid separates which melts at 166°: the author finds that this substance is a mixture of two isomerides which he terms respectively α- and β-*dioxyazobenzene* (or *azobenzene-dioxybenzene*). The two differ in their solubility in alcohol, and can thus be separated; the α body is readily soluble in alcohol, ether, acetic ether, chloroform, and benzene, but insoluble in water, which precipitates it from alcoholic solution in small red needles: it is soluble in dilute alkalis, and precipitable from the solutions unchanged by means of acids: it melts at 161°. The β-compound is formed in much less quantity; it melts at 215° (not corrected), resembles the α-modification, but is only sparingly soluble in cold alcohol, though readily soluble in hot spirit. The analytical numbers lead to the formula $C_6H_5—N{=}N—C_6H_3(OH)_2$ for both substances. On dissolving α-dioxyazobenzene in glacial acetic acid and adding excess of bromine, a magma of crystals results consisting of the tribromo-derivative, fusing at 186°: long-continued contact with the acid and bromine, or boiling for a short time, breaks up this brominated body, forming *tribromoresorcin* (just as diazobenzene itself splits up): thus $C_6H_5—N{=}N—C_6Br_3(OH)_2 + H_2O = C_6H_5.OH + C_6HBr_3(OH)_2 + N_2$; the phenol thus produced is converted into bromophenol by the excess of bromine present.

When orcin is substituted for resorcin in the above experiment, *methyl-dioxyazobenzene* (*azobenzene-dioxymethylbenzene*) is produced, indicated by the formula $C_6H_5—N{=}N—C_7H_5(OH)_2$; like dioxyazobenzene, this substance possesses great tinctorial power; it melts at 183°, and is soluble in alcohol, ether, chloroform, and alkalis, being precipitated from the latter solution by acids, and from its solution in glacial acetic acid by water. On bromination, a dibromo-derivative melting at 183° is formed.

Alpha-naphthol gives rise to a similar derivative, probably to two isomerides, one more soluble in alcohol than the other. The more soluble substance, *azobenzene-α-naphthol*, does not crystallise readily; it has powerful tinctorial properties: acids dissolve it, forming solutions which are decolorised by nascent hydrogen. Brominated derivatives could not be formed, the body being decomposed by bromine: sulphuric acid appears to form a sulphonic acid not yet obtained pure.

C. R. A. W.

Action of Sulphurous Acid and the Sulphuric Acids upon Diazo-compounds. By W. KONIGS (*Deut. Chem. Ges. Ber.*, x, 1531—1534). By the action of aqueous sulphurous acid upon a solution of diazobenzene sulphate or chloride, a compound is obtained which, both in its properties and constitution, the author shows to be identical with the hydrazine derivative—$C_6H_5.NH.NH.SO_2C_6H_5$, which Fischer prepared by the action of benzenesulphochloride upon phenylhydrazine. The course of the reaction appears to be—(1) the conversion of a portion of the diazobenzene into benzenesulphinic acid, which (2), unites with the undecomposed diazobenzene; and (3), the reduction of the product of this union by the sulphurous acid.

In order to substantiate his deduction, the author has tried the action of sodium benzenesulphinate upon diazobenzene nitrate, and found in effect that a body corresponding in composition with diazobenzene benzenesulphinate—$C_6H_5N{=}N.SO_2.C_6H_5$—is formed. It melts at 75—76°, it is insoluble in water in the cold, but soluble in alcohol, ether, and benzene. Its constitution is regarded by the author as that of a phenyl-diazophenylsulphone, $SO_2{<}\begin{smallmatrix}C_6H_5\\N_2.C_6H_5\end{smallmatrix}$. By the action of reducing agents it is converted into the hydrazine-derivative first described.

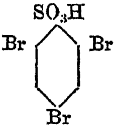
The yellow potassium diazobenzenesulphonate, $C_6H_5N.N.SO_3K$, is also converted, by reduction, into a hydrazine-derivative, the colourless body, $C_6H_5.NH.NH.SO_3K$.

The three compounds described in this paper all yield on treatment with mercuric oxide, according to Fischer's method, crystals of the yellow diazobenzenebenzolsulphinate.

The author is engaged in the experimental generalisation of these observations. C. F. C.

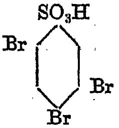
Decomposition of Substituted Benzene-sulphonic Acids by Water and by Acids at High Temperatures. By H. Limpricht (*Deut. Chem. Ges. Ber.*, x, 1538—1542).—Para- and meta-dibromobenzenesulphonic acids are completely resolved by the action of concentrated HBr at temperatures of 250° and 180° respectively, into sulphuric acid and the corresponding dibromobenzene. The ortho-acid is similarly, but only partially decomposed at 250°.

Tribromobenzene-sulphonic acid,



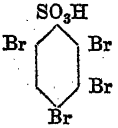
, is completely resolved by the action of concentrated HCl at 150° into sulphuric acid and tribromobenzene (m.p. 118·5°).

Tribromobenzene-sulphonic acid,

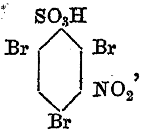


, is decomposed by concentrated HBr at 200° into sulphuric acid and tribromobenzene (small needles; m.p. 140°).

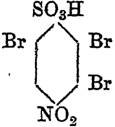
Tetrabromobenzene-sulphonic acid,

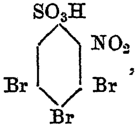


, heated with concentrated HBr or HCl to 150°, forms sulphuric acid and tetrabromobenzene (m.p. 98·5°).

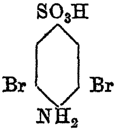
Nitrotribromobenzene-sulphonic acid, 

, is resolved by concentrated HCl at 185°, for the greater part, into sulphuric acid and nitrotribromobenzene (m.p. 125°).

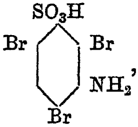
The isomeric acid, 

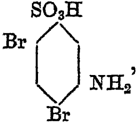
, is decomposed at 220°, with evolution of red vapours and formation of a body crystallising from alcohol in small needles which melt at 53°, which, however, is not nitrodibromobenzene. The behaviour of the third isomeride, 

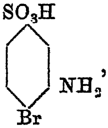
, is similar; the product of the decomposition, although crystallising in beautiful needles, is a mixture of compounds melting between 149° and 230°.

Dibromamidobenzene-sulphonic acid, 

, is decomposed by heating with water to 150°, with formation of sulphuric acid and two isomeric dibromanilines (melting points 70° and 84° respectively); tribromaniline and bromaniline are also formed, probably by the action of sulphuric acid upon the dibromanilines.

Tribromamidobenzene-sulphonic acid, 

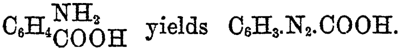
, is rapidly converted by heating with water, at 150°, into the dibromamidobenzene sulphonic acid, 

, which, at 250°, is resolved first into bromamidobenzene-sulphonic acid, 

, and finally into metamidobenzene-sulphonic acid.

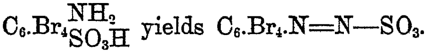
In this case, therefore, bromine, and not the SO_3H group, is replaced by hydrogen.
C. F. C.

Structure of the Diazo-compounds of Benzenesulphonic Acids. By H. LIMPRICHT (*Deut. Chem. Ges. Ber.*, x, 1534—1538).—From the fact that the ethyl ether of amidobenzoic acid, $C_6H_4.NH_2.CO.OC_2H_5$, yields a corresponding diazo-compound, which must be constituted according to the formula, $C_6H_3.N_2.COOC_2H_5$, Griess has shown (*Ber.*, ix, 1653) that diazobenzoic acid is formed from amidobenzoic acid by the substitution of one N-atom for the two H-atoms of the NH_2 molecule and of 1 H-atom of the benzene nucleus, thus:—



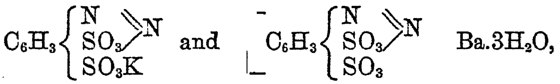
$$C_6H_4{}^{NH_2}_{COOH} \text{ yields } C_6H_3.N_2.COOH.$$

The author has investigated the applicability of similar reasoning to the analogous diazo-derivatives of benzenesulphonic acid. He finds that they are incapable of forming compounds with acids. He also failed in attempts to prepare the ethyl ether of amidobenzenesulphonic acid, and therefore to solve the problem by Griess's method of determining the constitution of diazobenzoic acid. Beckurts, however, by preparing the diazo-derivative of tetrabromobenzenesulphonic acid from the corresponding amido-acid (*Ber.*, ix, 479), has supplied the necessary proof that the hydrogen atoms replaced in this conversion are those of the NH_2 and SO_3H groups, thus:—

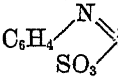


$$C_6.Br_4{}^{NH_2}_{SO_3H} \text{ yields } C_6.Br_4.N{=}N{-}SO_3.$$

This view is much strengthened by a further observation of the author's, viz., that by the action of nitrous acid upon the aqueous solutions of the neutral potassium and barium salts of β-amidobenzenesulphonic acid, the same diazo-compounds are formed as from the corresponding acid salts: these are respectively:—



$$C_6H_3\left\{\begin{array}{l}N\diagdown\\ SO_3\diagup\!N\\ SO_3K\end{array}\right. \text{ and } C_6H_3\left\{\begin{array}{l}N\diagdown\\ SO_3\diagup\!N\\ SO_3\end{array}\right. Ba.3H_2O,$$

i.e., that diazo-compounds derived from the neutral salts of benzenedisulphonic acid, do not exist, and hence a serious objection to the formula  $C_6H_4\langle N{=}N\text{—}SO_3\rangle$, as representing the constitution of diazobenzenesulphonic acid is removed. C. F. C.

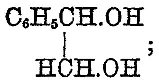
Action of Sulphuryl Chloride on Resorcin. By G. REINHARD (*Deut. Chem. Ges. Ber.*, x, 1524—1525).—Dubois found some years since (*Jahrb.*, 1866, 283), that, by the action of sulphuryl chloride upon phenol, two monochlorophenols, hydrochloric acid and sulphuric anhydride were formed. The author has extended this observation to resorcin, and obtains, by the action of sulphuryl chloride upon this body, a compound of the formula $C_6H_4Cl_2O_2$. It is easily soluble in water, alcohol, and ether, melts at 100° to a clear liquid, and at a higher temperature may be distilled unchanged. Whether the constitution of this body is that of resorcin in which the hydrogen of the OH-molecules is replaced by chlorine, the author is not yet in a position to state. C. F. C.

On certain Pinacones and Pinacolins. By W. THÖRNER and TH. ZINCKE (*Deut. Chem. Ges. Ber.*, x, 1473—1477).—1. *Benzpinacone*, $C_{26}H_{22}O_2$ (m.p. 185—186°).—This compound, on fusion or distillation, is not converted into a physical isomeride, as stated by Linnemann, but is decomposed into benzophenone and benzhydrol, thus:—$C_{26}H_{22}O_2 = C_{13}H_{10}O + C_{13}H_{12}O$. The decomposition is complete even at the fusion temperature of the pinacone. Alcoholic potash effects the same resolution: Linnemann's observation, therefore, of the production of benzhydrol by the action of sodium-amalgam on the alcoholic solution of the pinacone, is probably referable to this cause. Benzpinacone is usually regarded as tetraphenylglycol, $(C_6H_5)_2.OH.C—C.OH.(C_6H_5)_2$: all attempts, however, to demonstrate the presence of two OH—mol., by the formation of mixed ethers, have proved unsuccessful. Benzpinacone is converted into the corresponding pinacoline by the action of acids and chloranhydrides. By acetic anhydride, however, it is resolved into benzophenone and benzhydrol. Benzpinacoline is somewhat soluble in hot alcohol, and crystallises from this solution, on cooling, in small shining needles; these melt at 178—179° to a colourless liquid which cools to an amorphous mass. It is further soluble in benzol, chloroform, and carbon disulphide, and also to some extent in ether. The constitution of this body is probably the following:—$(C_6H_5)_3C—CO—C_6H_5$.

2. *Tolylphenylpinacone*, $C_{28}H_{26}O_2$, (m.p. 164—165°).—Closely resembles the preceding in physical properties, and in undergoing, at its point of fusion, resolution into tolylphenyl ketone and the corresponding hydrol, thus:—$C_{28}H_{26}O_2 = C_{14}H_{12}O + C_{14}H_{14}O$. By the action of chromic acid it is decomposed according to the equation, $C_{28}H_{26}O_2 + O = 2C_{14}H_{12}O + H_2O$. Compound ethers of this body, also, could not be obtained.

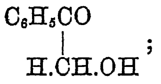
The corresponding pinacoline occurs in two modifications. β-Tolylphenylpinacoline (m.p. 136—137°), which is the more stable, results from the action of acetyl and benzoyl chlorides, and of concentrated acetic and hydrochloric acids upon the pinacone. The α-modification is obtained in the pure state by adding hydrochloric acid to the alcoholic solution of the pinacone, and leaving it for some time at the ordinary temperature. By the action of acetic and benzoic anhydrides, on the other hand, the pinacone is decomposed in the manner described above. From their observations on this pinacone the authors conclude that pinacones are formed as intermediate products in the production of pinacolins from ketones. C. F. C.

Styrolene Alcohol (Phenyl-glycol). By P. HUNÄUS and TH. ZINCKE (*Deut. Chem. Ges. Ber.*, x, 1486—1491).—Phenyl-glycol is found by the authors to yield on oxidation successively benzoyl-carbinol and formobenzoic acid; thus:—



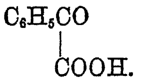
$$\begin{array}{c} C_6H_5CH.OH \\ | \\ HCH.OH \end{array};$$

Phenylglycol.



$$\begin{array}{c} C_6H_5CO \\ | \\ H.CH.OH \end{array};$$

Benzoylcarbinol.



$$\begin{array}{c} C_6H_5CO \\ | \\ COOH. \end{array}$$

Formobenzoic acid.

The oxidation of the secondary alcohol-group, therefore, precedes that of the primary.

Benzoyl carbinol, $C_6H_5CO.CH_2OH$, crystallises from its solution in alcohol and in ether, in large six-sided tables; from its aqueous solution in large shining plates which retain water. These latter melt at 73—74°, the anhydrous modification at 86°. This body is a powerful reducing agent, probably by reason of its tendency to decomposition according to the equation:—

$$C_6H_5COCH_2OH = C_6H_5COH + HCOH.$$

The *acetic ether*, $C_6H_5COCH_2OC_2H_3O$ (m.p. 49°), and the *benzoic ether*, $C_6H_5CO.CH_3.O.C_7H_5O$ (m.p. 117°), of this carbinol are described.

Formobenzoic acid, $C_6H_5CO.COOH$, has also been prepared by oxidizing mandelic acid, $C_6H_5CH.OH.COOH$, with nitric acid. The barium and silver salts of the acid are described.

The strongly reducing properties of benzoyl carbinol seem rather to indicate that its constitution is that of mandelic aldehyde, C_6H_5—CH.OH—COH. That this view, however, is incorrect, follows from the fact that by the action of silver benzoate upon the chloride of methylphenyl ketone, $C_6H_5.CO.CH_2Cl$, a benzoic ether is obtained which is identical with that described above. The constitution of benzoylcarbinol is thus established. In conclusion, the authors express the opinion, that the reducing properties of many complicated bodies, which are assumed to be aldehydes, possessing the characteristic COH-group, may be referred to the presence of this same $CO.CH_2OH$-group.

C. F. C.

Compounds of Salicylic Acid with Albuminoïds. By FR. FARSKY (*Chem. Centr.*, 1877, 148).—The author has prepared compounds of egg-albumin, casein, fibrin, and syntonin with salicylic acid by several methods. Either the albuminoïd and the acid were mixed together and allowed to stand with constant stirring, or the two were combined in a dialyser, or the vapour of the acid was made to act on the finely powdered substance. Whichever method of preparation was adopted, the solid substance was finally extracted by pure ether, which was shaken up with it as long as the filtrate gave a reaction with ferric salts. The albumin-compound was then washed with hot water, and dried in an air-bath at 120—130°.

Analyses showed that on the average 14·16 per cent. of salicylic acid was combined with 85·84 per cent. of the albuminoïd, which points to the formula $C_{72}H_{112}N_{18}SO_{22} + 2C_7H_6O_3$. These compounds are found to be quite as easily digestible as the uncombined albuminoïds, so that salicylic acid might possibly be used for the preservation of feeding-stuffs.

In connection with the above researches the author has been enabled to make a more accurate investigation of salicylic acid, and he gives the following account of it. It crystallises from concentrated solutions in slender, almost colourless needles, from dilute solutions in larger prismatic, very hard crystals, often very prettily grouped. If, however, other bodies are present in the solution, and more especially if they are organic bodies, regular crystals are not formed, but, according to the nature and quantity of the admixed body, either crescent-shaped, annular, or tufted forms which scarcely resemble crystals, are obtained.

When the foreign body is removed the acid gradually regains the capability of forming acicular crystals. Freezing the solution also brings about the change. The acid melts at 157·5°, and sublimes at 200°, but even at 80° a considerable quantity volatilises. Perfectly pure crystals may be obtained by heating a solid body containing the acid, or a solution of the acid, at this temperature in the air- or water-bath. The acid, as is well known, splits up on boiling into carbon dioxide and phenyl-alcohol; but it is quite sufficient to heat the solution of the acid or certain salts, especially in presence of other acids, for a long time on the water-bath, to bring about this change. Hydrated sulphuric acid decomposes salicylic acid only when it is added all at once to the solid acid or its solution.

Permanganate of potassium, especially in presence of sulphuric acid, oxidises salicylic acid, and among other products of the decomposition are found formic and carbonic acids and water. A similar decomposition is effected by boiling the acid with potassium bichromate and sulphuric acid. If the solution of the acid is heated with the bichromate without addition of sulphuric acid, a body passes over with the steam which has an unpleasant odour; it has not been examined. When salicylic acid is brought into contact with ferric acetate, it combines with the iron, the liquid becomes of a violet colour, and deposits a dirty violet precipitate of $Fe_2H_2O_4$.

This hydrate dissolves in water and forms a golden-yellow liquid, which can be concentrated, but is decomposed by contact with acids, bases, salts, alcohol, ether, and even filter-paper, and rendered insoluble. If, however, the solution of the ferric salt is tolerably concentrated, and especially if the mixed solution is not too acid, a brown salicylate separates out. The acid behaves in a similar way to lead acetate; lead salicylate is formed, and very strong vapours of acetic acid are evolved in the cold.

Salicylic acid forms three salts with ferric oxide, a normal salt, a basic salt, and a so-called ferric ferro-salicylate.

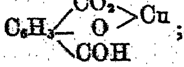
Compare the author's paper on the "Application of these salts to acidimetry and alkalimetry" (*Wien. Sitzungsber*, lxxiv, 49).

G. T. A.

Ortho- and Para-aldehydosalicylic Acids, Ortho-aldehydoparoxybenzoic Acid, and the Phenoldicarboxylic Acids thence obtained. By Ferd. Tiemann and K. L. Reimer (*Deut. Chem. Ges. Ber.*, x, 1562—1576).—The authors give further details as to the preparation of the acids produced by the action of chloroform on strongly alkaline solutions of salicylic and paroxybenzoic acids: the best yield is obtained by dissolving 30 grams of salicylic (or paroxybenzoic) acid in 100 c.c. of caustic soda solution of sp. gr. 1·35 (containing about 43 grams of sodium hydroxide), and cohobating with 5—10 grams of chloroform, further quantities of the last substance being from time to time added (20—25 grams in half an hour). When a little chloroform condenses and drops back, more caustic soda-solution is added, so that in the course of 4 to 5 hours about 150 c.c. of the soda-solution and 45—46 grams of chloroform have been used altogether: no appreciable increase in the yield is noticed after this period.

The resulting deep-red liquid is cautiously neutralised with hydrochloric acid, whereby a dark resinous decomposition-product is thrown down: the filtrate is strongly acidulated with hydrochloric acid, and the resulting liquid (containing in suspension a white precipitate) agitated with ether; the concentrated ethereal extract is then shaken with 100 c.c. of solution of sodium-hydrogen sulphite of sp. gr. 1·35, diluted with 40—50 c.c. of water; this quantity suffices to take up all the aldehydo-bodies found. By means of sulphuric acid and steam (40 grams concentrated acid diluted with 40 c.c. of water) the sulphite compounds are decomposed, the whole being thrown on a filter after cooling to 60°. If paroxybenzoic acid is used in the first instance, *ortho-aldehydo-paroxybenzoic acid* remains on the filter, a little more of this acid being contained in the filtrate together with a little *paroxybenzoic aldehyde;* the yield of the aldehydo-acid is about 20 per cent. of the paroxybenzoic acid employed. If salicylic acid was originally employed, *para-aldehydo-salicylic acid* remains on the filter, the filtrate containing small quantities of the same, together with *ortho-aldehydo-salicylic acid. Salicylic aldehyde* is also produced in small quantity when the sodium hydrate solution originally used was more dilute than that recommended, and especially if the mixture was not heated to a higher temperature than the boiling point of chloroform, a large quantity of that substance being added at first: this product is easily isolated by distillation with steam, the quantity not exceeding 1 or 2 per cent. of the salicylic acid used: possibly it is formed by the splitting up of the salicylic acid into phenol and carbon dioxide, the former being then aldehydated; or possibly it is produced by the decomposition of the ortho-aldehydo-salicylic acid; or, again, and more probably, it may result from a direct exchange of carboxyl for aldyl (the group COH characteristic of aldehydes).

To separate ortho- and para-aldehydo-salicylic acids, the method formerly described (methodical crystallisation) does not suffice, traces of the para-acid being always retained by the ortho-acid thus prepared. The following process answers well:—The solution of the mixed acids is shaken with ether, the ethereal extract evaporated, and the residue dissolved in considerably diluted ammonia-liquor: copper sulphate solution is then added, and sufficient ammonia to dissolve a portion of the precipitate with a blue colour; the whole is then heated to boiling, when almost the whole of the ortho-acid separates as a basic copper salt of a bright green colour, containing when dried at 100°,



$C_6H_3\begin{cases} CO_2 \\ O \\ COH \end{cases}$ with CO_2 and O joined $>Cu$

; on treatment with dilute hydrochloric acid, this salt furnishes pure ortho-aldehydo-salicylic acid, crystallising from water in fine interlaced needles resembling salicylic acid, and melting at 179° when perfectly pure (166° was given as the melting point in a former paper): by careful heating it can be sublimed unchanged, but if quickly heated to 220° in the fused state, it splits up into carbon dioxide and salicylic aldehyde: when crystallised it is represented by the formula $C_8H_8O_4,H_2O$; the crystals becoming anhydrous at 100°. Alcoholic solutions of the acid exhibit a feeble bluish-violet fluorescence: in caustic soda it dissolves with a yellow colour. Ferric chloride strikes a red tint, and sodium carbonate dissolves the acid with effervescence.

Two classes of salts are formed by each one of the three aldehydo acids, viz., neutral salts, and basic salts in which the phenolic hydrogen is also replaced; the points at which the neutral salts are formed with alkalis and the two salicylic derivatives are easily determined by means of litmus, a red coloration being given to the litmus as long as the amount of alkali added is less than that requisite to form the neutral salt, and a blue with the slightest excess: with the paroxybenzoic derivative, however, the point of neutrality cannot be thus determined, as the litmus becomes green before the amount of alkali requisite to form the neutral salt is added; further addition of alkali deepens the green, but there is no characteristic colour change marking the point of neutrality. The alkaline salts of all these acids are very soluble, and crystallise only from extremely concentrated solutions; the neutral salts of the two salicylic derivatives are colourless by transmitted light, appearing to possess a green fluorescence with reflected light; traces of excess of alkali gives a yellow coloration. Tables of the reactions of the neutral and basic ammonium salts of the three acids with calcium and barium chlorides, silver nitrate, copper sulphate, and lead acetate are given, precipitates being formed in most cases either at once or on standing.

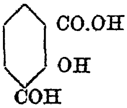
Ortho-aldehydo-salicylic acid dissolves in 1500—1600 parts of water at 23—25°, and in 15—16 parts at 100°; para-aldehydo-salicylic acid in 2600—2700 parts at 25°, and in 145—150 parts at 100°; ortho-aldehydo-paroxybenzoic acid is slightly more soluble in cold water than the latter.

When fused with 10—15 parts of potassium hydroxide these three aldehydo-acids are readily converted into the corresponding phenol-dicarboxyl acids, 6 to 8 minutes' fusion sufficing with potash to which a little water has been added (temperature of fusing mixture not stated). On cooling, solution in water, and addition of hydrochloric acid, the dicarboxyl acids are mostly precipitated, the remainder being readily obtainable by shaking with ether. No "molecular interchange" takes place during the fusion, as the same acids respectively are produced by oxidising the aldehydo-acids with permanganate in alkaline solution. To effect this oxidation, 1 part of aldehydo-acid is dissolved in a little caustic soda, and 200—250 parts of water are added; 3—4 parts of solid potassium permanganate are then thrown in, and the whole left for 16—24 hours with occasional stirring: the liquid is then heated to boiling, filtered off from precipitated manganic hydrate, and evaporated to a small bulk: on adding hydrochloric acid and shaking with ether, the dicarboxyl acids are extracted, together with unaltered aldehydo-acids, which are removed by agitating the ethereal liquids with sodium-hydrogen sulphite: finally the ether is evaporated off and the residue crystallised from water. In this way para-aldehydo-salicylic acid is the most oxidised, ortho-aldehydo-paroxybenzoic acid being much less completely converted, whilst only 1—2 per cent. of dicarboxyl acid is obtained from ortho-aldehydo-salicylic acid; a somewhat better result is obtained in the last case by substituting silver oxide for permanganate, a mirror being copiously deposited.

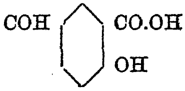
β-Phenoldicarbonic acid (*β-oxyisophthalic acid*) thus obtained from ortho-aldehydo-salicylic acid, crystallises with one molecule of water in hair-like white needles and well defined prisms: when air-dry it melts at 139°; when thoroughly dried at 100° at 243—244.° Watery and alcoholic solutions fluoresce blue-violet, the fluorescence disappearing on addition of caustic alkali; ferric chloride strikes a cherry-red tint. By cautiously heating, a little of the acid can be sublimed unchanged; the greater part, however, splits up into carbon dioxide and salicylic acid. It forms three classes of salts, acid, neutral, and basic; litmus is blued only when alkali is added in quantity just sufficient to form the neutral salt and a trace over. The solubility in water is 1 part in 35—40 of water at 100°, in 700 of water at 24°; in alcohol and ether it readily dissolves, less easily in chloroform.

α-Phenoldicarbonic acid (*α-oxyisophthalic acid*) is obtained by the oxidation of either para-aldehydo-salicylic acid or ortho-aldehydo-paroxybenzoic acid, a fact indicated by the formulæ:—

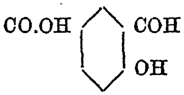
Ortho-aldehydo-salicylic acid.



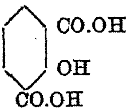
Para-aldehydo-salicylic acid.



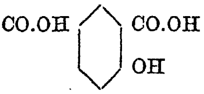
Ortho-aldehydo-paroxybenzoic acid.

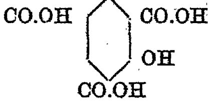


β-phenol-dicarbonic acid.



α-phenol-dicarbonic acid.



It is identical with the oxyisophthalic acid obtained some short time ago by Ost (*J. pr. Chem.*, N. F., xiv, 93; xv, 301), melting at 300°, and crystallising anhydrous. Ost obtained this acid along with oxytrimesic acid, , by treating salicylic acid with alkali and carbon dioxide; whence it should result that oxytrimesic acid is obtainable from either α- or β-oxyisophthalic acid. On comparing the reactions of oxytrimesic acid and these two acids (both as neutral and basic ammonia salts) with calcium and barium chlorides, magnesium sulphate, silver nitrate, and lead acetate (a table of which is given), it is noticeable that there is a greater resemblance between oxytrimesic acid and the β-oxyisophthalic acid, than between oxytrimesic acid and the α-oxyisophthalic acid. All three give cherry-red colorations with ferric chloride; the solubilities in water are: α-oxyisophthalic acid; 1 in 5000 at 10°, in 3000 at 24°, in 145—158·5 at 100°: β-oxyisophthalic acid; 1 in 700 at 24°, in 35—40 at 100°: oxytrimesic acid, 1 in 200 at 10°. By the action on salicylic acid of carbon tetrachloride in alkaline solution, experiments now in progress by G. Hasse show that there is formed not only α- but also β-oxyisophthalic acid. Reimer also finds that by hydrogenation these aldehydo acids are convertible into alcoholo-acids containing the group $CH_2.OH$: similarly Tiemann is investigating the acids formed by the action of chloroform on creosol (*homosalicylic* and *homoparoxybenzoic acids*), and the phenol dicarboxyl acid formed from meta-oxybenzoic acid.

C. R. A. W.

Action of Dehydrating Agents upon Acid Anhydrides. By S. Gabriel and A. Michael (*Deut. Chem. Ges. Ber.*, x, 1551—1562). —The authors have improved their method for the preparation of phthalylacetic acid by the action of phthalic anhydride upon a mixture of acetic anhydride and anhydrous sodium acetate. The constitution of the acid is expressed by the formula $C_6H_4{<}{\substack{CO\\CO}}{>}CH.CO.OH$, and is deduced from a consideration of a number of its reactions:—

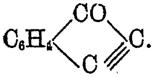
1. If the acid is dissolved to a neutral solution by cold caustic potash it is precipitated from this solution unchanged on the addition of hydrochloric acid, but if the alkali be added in excess the addition of the acid causes no precipitation; the alkaline solution, however, on standing, deposits a crystalline body, which occurs in shining needles melting at 90°, and is shown on investigation to be phthalylacetic acid + 2 mol. H_2O, and to be constituted according to the formula $\left.C_6H_4{<}{\substack{COOH\\CO.CH_2.COOH}}\right\} + H_2O$. It may therefore be designated *benzaceto(ortho)carbonic acid.* By boiling the aqueous solution of this acid it is converted, with loss of $CO_2 + H_2O$, into a monobasic acid, a crystalline compound melting at 114—116°, which is found to be *acetophenone(ortho)carbonic acid,* $C_6H_4{\substack{CO.CH_3\\COOH}}$. This same acid is obtained directly from phthalylacetic acid by heating the latter with water to 200°.

2. By the action of bromine on phthalylacetic acid in presence of glacial acetic acid, a body is obtained crystallising in long colourless needles which melt at 160°. Its composition is expressed by the formula $C_9H_5Br_3O_3$. It is completely decomposed by alkalis according to the equation $C_9H_5Br_3O_3 + H_2O = CHBr_3 + C_8H_6O_4$. From this resolution it is concluded to be *tribromacetophenone(ortho)carbonic acid,* $C_6H_4{\substack{CO.CBr_3\\CO.OH}}$.

The decomposition in question is similar to that of pentabromacetone by ammonia into *bromoform* and *dibromacetamide.* The action of chlorine upon phthalylacetic acid under the same conditions is entirely analogous; the resulting trichloracetophenone(ortho)carbonic acid melts at 144°.

3. By dissolving phthalylacetic acid in ammonia and adding hydrochloric acid to the solution, a white precipitate is obtained, which is somewhat soluble in hot water, separating from this solution on cooling in colourless silky needles (m. p. 200°). This body is shown to be *phthalylacetamide*, $C_6H_4(CO)_2.CH.CO.NH_2$.

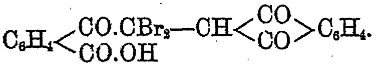
4. By the action of concentrated sulphuric acid upon phthalylacetic acid a compound is obtained crystallising in slender yellow needles, which are soluble in nitrobenzene but not in alcohol, ether, nor in glacial acetic acid. The same body is obtained, but in very small quantity, as a by-product in the preparation of phthalylacetic acid. For the constitution of this body the authors propose the formula



5. As products of reduction of phthalylacetic acid, by means of sodium-amalgam two crystalline bodies are obtained, melting respectively at 173—175° and 150—151°; of these, however, the first passes on fusion into the second, with which it is indeed isomeric. Their empirical composition is represented by the formula $C_{10}H_8O_4$. The first is a bibasic acid, probably *cinnamorthocarbonic acid*, the latter a monobasic acid, and at the same time probably an anhydride of *benzhydrylacetorthocarbonic acid.*

The authors have further investigated the action of sodium acetate upon a mixture of phthalic anhydride and succinic acid; this they find to yield a compound crystallising in long yellow needles, which melt at a temperature above 350°. This body is soluble in aromatic liquids of high boiling point: its constitution is that of *ethinorthophenylenediketone* or *ethindiphthalyl*, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>CH—CH<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_4$, indicating therefore that it is a product of the condensation of phthalic and succinic anhydrides.

In contact with aqueous alkalis at 100° it is converted, by the addition of 2 mol., H_2O, into (ortho) *phenylethyleneketonecarbonic acid*, $C_6H_4<\genfrac{}{}{0pt}{}{CO—CH_2—CH_2—CO}{COOH\qquad\quad HO.OC}>C_6H_4$, crystallising in prisms which melt at 166° and are freely soluble in alcohol. By the action of bromine at 100° on ethindiphthalyl in presence of acetic acid, two of its H-atoms are replaced by bromine, and by the simultaneous addition of 1 mol., H_2O, is converted into the compound—



$$C_6H_4<\genfrac{}{}{0pt}{}{CO.CBr_2—CH<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_4.}{CO.OH\qquad\qquad\qquad\qquad}$$

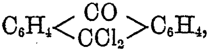
This body crystallises in colourless, shining octohedrons, which melt at 285—287°, and are soluble in alcohol. C. F. C.

Trimellitic Acid. By G. KRINOS (*Deut. Chem. Ges. Ber.*, x, 1491—1495).—By the regulated oxidation of xylidic acid by means of potassium permanganate in alkaline solution, the author has succeeded in realising its conversion into trimellitic acid, according to the equation—

$$C_6H_3(CO_2K)_2CH_3 + 2KMnO_4 = C_6H_3(CO_2K)_3 + KOH + H_2O + 2MnO_2.$$

Since the (1, 2, 4) position of the substituting groups in the former acid has been established beyond doubt, a similar constitution must be assigned to the derived acid. The view expressed by Baeyer some eight years since of the constitution of trimellitic acid is thus experimentally corroborated.

Isophthalic acid also occurred as a product of the oxidation of xylidic acid, resulting most probably from the removal of CO_2 from the molecule of trimellitic acid. C. F. C.

Conversion of o-Benzyltoluene-derivatives into Anthracene-derivatives. By W. THÖRNER and TH. ZINCKE (*Deut. Chem. Ges. Ber.*, x, 1477—1481).—By the action of chlorine upon liquid tolylphenyketone, $C_6H_5—CO—C_6H_5.CH_3$, the authors obtain an anthraquinonedichloride,  $C_6H_4<\substack{CO \\ CCl_2}>C_6H_4$, crystallising from its solution in benzene in the form of brilliant transparent prisms, which melt at 132—133°. In presence of water it is at once decomposed into anthraquinone and hydrochloric acid. It is dissolved unchanged in the cold by absolute alcohol and by glacial acetic acid, but on warming these solutions complete decomposition of the chloride into anthraquinone ensues: hence the formula for this body given above.

The dichloride is attacked by PCl_5 at a temperature of 150—160°, with formation of a tetrachloride, $C_{14}H_8Cl_4$, crystallising from ether in small colourless needles, which melt at 203—204°: their solutions exhibit a beautiful blue fluorescence. By the action of PCl_5 upon *o*-benzyl- and *o*-benzoyl-benzoic acids chlorinated derivatives of anthraquinone are obtained. These the authors have not yet investigated. C. F. C.

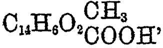
Nitro-alizarin. By A. ROSENSTIEHL (*Ann. Chim. Phys.* [5], xii, 519—529).—The author has studied the action of nitrous fumes on alizarin, which was first observed by Strobel, namely, that when a piece of cloth, printed or dyed with garancin or artificial alizarin-red, is dipped into a flask filled with nitrous fumes, the colour is changed to orange, which is not attacked by soap. When alizarin paste is treated with nitrous fumes, a portion is converted in a mononitroalizarin, which forms a sodium compound insoluble in alkalis; this substance, on decomposition with acids, yields a crystalline body which, according to its analysis, has the formula $C_{14}H_7(NO_2)O_4$. It is soluble in chloroform, from which it crystallises in orange-coloured plates, appearing green by reflected light. It is sparingly soluble in water, melts at 230°, and a little above this temperature sublimes, forming orange needles and yellow plates possessing a green reflection. The former body resembles alizarin in its properties, but its alkaline solution has a reddish-violet colour, whilst that of alizarin is coloured bluish-violet; their spectra closely resemble each other.

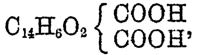
With calcium bicarbonate, nitroalizarin forms a precipitate which is not decomposed by carbon dioxide: by this means alizarin can be separated from nitro-alizarin, inasmuch as the precipitate formed by alizarin and calcium bicarbonate is decomposed by carbon dioxide with liberation of alizarin. The compounds of nitro-alizarin with bases are exceedingly stable; ferric oxide produces a fine black colour. On reduction nitro-alizarin yields an amido-compound.

When an alkaline solution of nitro-alizarin is treated with phosphorus, the colour changes first to blue, then to green, and finally to yellow; if the reaction be stopped when the liquid becomes blue, a body may be isolated which gives a garnet-red precipitate with alumina, but if it be allowed to proceed until the reduction is complete, a substance is obtained which gives a brown colour with aluminium mordants. Pseudo-purpurin, purpurin, and anthra-purpurin are bleached by nitrous fumes. L. T. O'S.

Methyl Derivatives of Anthracene. By C. Wachendorff and Th. Zincke (*Deut. Chem. Ges. Ber.*, x, 1481—1486).—From a substance closely resembling anthracene, obtained as a product of the action of a high-boiling aniline oil upon carbazol, the authors have isolated a hydrocarbon, $C_{16}H_{14}$, yielding on oxidation a quinone, $C_{16}H_{12}O_2$, and also two acids, a *mono-* and *di-*carbon acid, $C_{15}H_9O_2.COOH$ and $C_{14}H_6O_2(COOH)_2$. The hydrocarbon is therefore *dimethylanthracene*, $C_{14}H_8(CH_3)_2$. It is soluble in hot alcohol, benzol, and glacial acetic acid, and crystallises from these solutions on cooling in small, yellowish, shining plates, which melt at 224—225°, and may be readily sublimed.

Dimethylanthraquinone, $C_{14}H_6O_2(CH_3)_2$, is obtained, together with the COOH derivatives mentioned above, by long boiling of the hydrocarbon with glacial acetic and chromic acids. It crystallises from hot alcohol in small, bright, yellow needles, which melt at 155°, and sublime at higher temperatures in colourless feathery needles.

Methyl-anthraquinonecarbonic acid,  $C_{14}H_6O_2\genfrac{}{}{0pt}{}{CH_3}{COOH}$, crystallises from its solution in hot alcohol in snow-white flocks. It melts at 244—246°, and sublimes at higher temperatures.

Anthraquinonedicarbonic acid,  $C_{14}H_6O_2\left\{\begin{matrix}COOH\\COOH\end{matrix}\right.$, occurs in indefinite crystalline masses, which melt at a temperature exceeding 300°. It is much less easily soluble in alcohol, ether, and benzene than the preceding acid. By fusion with potash alizarin appears to be formed.

The oxidising action of chromic acid upon the hydrocarbon is of a variable nature, and yields, in addition to the compounds named above, products which result from the replacement of one or both methyl-groups by hydrogen. In one experiment dimethylanthracene was found to be oxidised directly to anthraquinone.

The authors have further isolated from certain aniline residues a hydrocarbon which appears to be *methyl-anthracene*, $C_{14}H_9.CH_3$. It crystallises from its solution in hot alcohol in yellowish shining plates, which melt at 208—210°. On oxidation with chromic acid it yields a quinone, which crystallises in small needles melting at 160—162°, and exhibits close resemblance to Fischer's methyl-anthraquinone (m. p. 162—163°).

As to the identity of the methyl-anthracenes described in this paper with compounds previously described as such, the authors are not prepared to pronounce definitely. C. F. C.

Juglone (Nucin). By C. REISCHAUER (*Deut. Chem. Ges. Ber.*, x, 1542—1548).—This body, prepared from the green shells of walnuts (*Juglans regia*), has been analysed by the author, who assigns to it the empirical formula, $C_{36}H_{12}O_{10}$.

A compound of this body with copper is obtained by adding its alcoholic solution to a solution of neutral cupric acetate either in water or alcohol. It occurs in small bronze-coloured shining crystals, and after drying at 100° contains 15·83 per cent. Cu. Sufficient data are not yet at hand for the determination of the constitution of these compounds.

This paper also contains details of certain modifications of the ordinary method of combustion which had to be adopted in the analysis of juglone, in consequence of its volatility. C. F. C.

Cantharadin and an Acid Derivative thereof. By J. PICCARD (*Deut. Chem. Ges. Ber.*, x, 1504—1506).—Three determinations of the vapour-density of cantharidin gave the numbers 6·36, 6·60, and 6·41; the empirical formula of this body is therefore $C_{10}H_{12}O_4$. It enters into complete fusion at 218°, and not at 250,° as usually stated.

By the action of hydriodic acid at a temperature of 100° in sealed tubes it is converted into a body, which, although possessing the same ultimate composition, differs essentially from cantharidin. It crystallises in needles, which melt at 278°, and are soluble in 12 parts boiling water; they are freely soluble in alcohol, slightly in ether, and insoluble in benzene. The solution of this body in glycerin does not blister the skin.

In its chemical properties it differs from cantharidin in being a strong acid, dissolving in and completely neutralising alkaline solutions, decomposing carbonates with effervescence, and being but partially expelled from its salts by acetic acid. The salts of *cantharic acid*, as this body is termed by the author, contain 1 atom of metal to 10 atoms of carbon; the union of the acid with bases is attended with the elimination of H_2O; it is therefore a monobasic hydrate; its equivalent, as determined by titration (cryst. oxalic acid = 63) is 196.

The general formula of its alkaline salts is $C_{10}H_{11}O_3.OR'$. The lead salt crystallises in long needles. Its formula is $(C_{10}H_{11}O_4)_2Pb$.

C. F. C.

Capsaicin. By J. C. THRESH (*Chem. Centr.*, 1877, 68—69).—By extracting powdered cayenne pepper with ether, evaporating the extract, dissolving it in hot alcoholic potash-lye, diluting the solution with water, and treating with barium chloride, a precipitate is obtained which, when washed, dried, treated with ether, and evaporated, leaves an oily red liquid, which Buchheim calls *capsicol*, exhibiting all the acrid properties of the fruit. Assuming this body to be a mixture, and knowing that castor oil, for example, renders other fatty oils more soluble in alcohol, the author dissolved the red oil in twice its volume of almond oil, and agitated this solution three times with strong alcohol. The acrid body was thus taken up by the alcohol, and the remaining oil was tasteless. The alcoholic extracts left a reddish-brown fatty mass having a strong pungent taste. This mass dissolves in dilute potash-lye, but forms a turbid soapy mixture with ammonia. By allowing the latter to stand for some time, numerous colourless prismatic crystals are obtained, which may be separated by filtration, washed, and dried. These crystals have a pungent taste, are but little soluble in cold water, more soluble in hot water, the solution giving a precipitate with strong acids. The peculiar behaviour of this substance, which the author calls *capsaicin*, led him to suppose that it was a fatty acid, which formed a soluble soap with potash, an insoluble soap with ammonia. This, however, was not correct, since pure crystals dissolved in potash gave, when treated with excess of ammonium chloride, a milky solution, which after some time yielded crystals of the pure substance. By boiling a solution of the crystals in absolute alcohol with sodium carbonate, filtering, and evaporating, an oily residue was formed, free from soda, which began to crystallise in a few days. This oily residue was quite insoluble in water (the formerly observed solubility was probably due to adhering traces of alkali). It was readily soluble in strong alcohol, the solution giving with barium and calcium chlorides precipitates which dissolved in ether. Silver nitrate forms a precipitate soluble in dilute ammonia. Ferric chloride forms a reddish precipitate when warmed. Dilute sulphuric acid and potassium bichromate destroy the pungent taste when heated with the substance. The same result is obtained with dilute nitric acid and potassium permanganate. The above reagents behave in a similar manner with capsicum preparations.

Capsaicin may be volatilised with ease without decomposition. It begins to volatilise at 100°. Water distilled from it has a pungent taste. Capsaicin may be isolated by dissolving the oil (capsicol) in dilute potash, treating the solution with ammonium chloride, collecting the precipitate, redissolving in potash, and treating it with ammonium chloride at 50°. The crystals obtained after a few days are, if necessary, treated once more in the same manner. The author has further obtained this substance in a pure state by dialysis. A few ounces of the concentrated tincture of cayenne pepper were poured into a dialyser of parchment paper and surrounded by strong alcohol. The latter absorbed the pungent constituent, and yielded, when evaporated, crystals agreeing with those formerly obtained. D. B.

Beer-yeast. By P. SCHÜTZENBERGER (*Chem. Centr.*, 1877, 73). —By boiling fresh yeast with water, and washing the boiled mass, a residue is obtained, the weight of which seems constant, varying only from 20 to 21·4 p. c. on the yeast used. But on agitating fresh yeast with water and exposing it to a temperature of 35—40°, the yeast loses 17—18 p. c. of soluble substances, while the undissolved portion after drying at 100° weighs 12·5 to 13 p. c. Fresh yeast therefore loses 8—9 p. c. of solid substances when treated with boiling water, and after digestion, 17—18 p. c. This fact depends on some physiological action that takes place in the substance of the yeast, and is not due to putrid fermentation. It may be further stated that this action does not go beyond a certain stage. The following method was used :—The digested yeast was boiled with much water, and filtered, and the slightly acid filtrate evaporated to a syrup on the water-bath, and then left to cool. The crystalline mass was then well boiled with 92 p. c. alcohol, whereby a pitch-like mass was separated, adhering to the sides of the flask. The alcoholic extract gave, when concentrated and cooled, a copious crystalline deposit, which, when washed and pressed, formed a white mass of crystals partly in the form of thin laminæ and partly as transparent globules. This crystallisation consisted almost entirely of pseudo-leucine with traces of tyrosine. The mother-liquor separated from the second crystallisation was heated over the water-bath to remove the alcohol; it was then diluted with water, treated with baryta-water in order to separate the phosphates; the filtrate was treated with carbonic acid to remove excess of baryta; and this second filtrate boiled with cupric acetate. The brownish flocculent precipitate formed was filtered off (it contained carnine, guanine, and xanthine in combination with cupric oxide), and the filtrate treated with alcohol in excess, when a bluish-white precipitate was obtained, soluble in water. After washing it with dilute alcohol, it yielded, on treatment with hydrogen sulphide, arabin combined with baryta, which was removed with sulphuric acid. The filtrate from the bluish-white precipitate, after being freed from alcohol, was treated with hydrogen sulphide, and the filtrate evaporated to a syrup, which on cooling solidified to a crystalline mass. By treating the latter with cold alcohol, leucine free from sulphur was obtained, probably containing butalanine. By evaporating the alcoholic liquid, a nitrogenous syrupy mass of a sweet taste was obtained. The above-mentioned precipitate of copper was washed with hot water and treated with hot dilute hydrochloric acid, the solution depositing on cooling a large proportion of the copper-compound. This deposit was decomposed by hydrogen sulphide, whereby carnine was obtained. The mother-liquor gave, after removing the copper and concentrating, crystals of xanthine hydrochloride, then crystals of guanine. Sarcine was obtained by precipitating the nitric acid solution of the first copper precipitate with ammonia and silver nitrate, washing with ammoniacal water, crystallising from hot nitric acid (12° Bé), and decomposing the silver-compound with sulphuretted hydrogen. The pitch-like residue mentioned above gave, when dissolved in hot water, crystals of tyrosine, which were further purified with acetate of lead, precipitation, and decomposition with hydrogen sulphide. Urea, uric acid, creatine, and creatinine, also inosite and inosinic acid, were absent. D. B.

Lacto-protein. By O. HAMMARSTEN (*Chem. Centr.*, 1877, 39).—Millon and Commaille maintained that, after precipitation of the casein and albumin of cows' milk, a third incoagulable albuminous substance could be obtained by addition of mercuric nitrate. Biel has since confirmed this statement for mares' milk. The author shows that the so-called lacto-protein is nothing more than a mixture of casein, acid-albumin, and probably traces of peptone. (See Kühne, *Lehrb. der Physiol. Chem.*, 568.) G. T. A.

Physiological Chemistry.

Employment of Compressed Oxygen in Physiological Investigations. By P. Bert (*Compt. rend.*, lxxxiv, 1130—1133).—Some years ago the author showed that all forms of organic life were rapidly destroyed when submitted to the action of compressed oxygen under considerable pressure. Continuing his researches on this subject, he has ascertained that the action of this reagent offers a means of distinguishing between the different varieties of fermentation, namely, those which depend upon the presence of a living growth, such as the acetic, alcoholic, and putrefactive fermentations, and those in which the action is due to some dissolved substance, such as diastase, pancreatin, or emulsin; in the former case the action of the gas immediately arrests fermentation, in the latter it is wholly ineffective.

Ripening of Fruit.—Fruits which under ordinary conditions are capable of ripening after being gathered, may be preserved for an indefinitely long time if submitted to the action of compressed oxygen for a few hours, but after having been so treated, they unfortunately cease to ripen. On the other hand, fruits which become mouldy on keeping, undergo this modification in compressed oxygen, and with greater rapidity even than in ordinary air: hence it is concluded (i) that ripening is the resultant of a cellular evolution; (ii) that rotting is due to the action of a soluble ferment, or to the direct oxidation of certain unknown substances.

Virus.—Fresh vaccine lymph and pus, submitted for a week to the action of oxygen under 50 atmospheres pressure, preserved their qualities unchanged; it is probable, therefore, that they do not owe their virulent properties to the presence of living cellules. In like manner, blood in a peculiar state of decomposition, termed *sang de rate* and *sang charbonneux*, which, according to the experiments of Davaine, is due to the development of bacteria therein, resisted altogether the action of the gas, as shown by the fact that several small animals rapidly succumbed after having been inoculated from each other in succession. The toxic principle of this blood is also precipitable by alcohol after the manner of diastase, and the coagulum retains its poisonous properties unaltered; so active, indeed, is the fermentative principle, even after partial isolation and precipitation by alcohol, that the blood of one poisoned animal is capable of causing death through many successive generations by continuing the inoculation as before mentioned. The author considers it premature to attempt any direct explanation of these latter experiments; he merely states that there exists in this virulent blood a poisonous principle which resists the action of compressed oxygen and alcohol, and which is, on the other hand, capable of being isolated after the manner of many soluble ferments.

J. W.

The Colouring Matter of Blood. By A. Jäderholm (*Zeitschr. f. Biologie*, xiii, 193, 255).—On treating blood with concentrated soda-solution, there is obtained after some time a bright red solution of reduced hæmatin, which subsequently coagulates. By dissolving this in water and treating it with dilute acetic acid, the colouring-matter is precipitated as oxyhæmatin. It may be somewhat purified by dissolving in ammonia water, and reprecipitating with acetic acid; but it still contains albumin and a chlorinated compound insoluble in water.

Hæmatin, though usually insoluble in dilute as well as in concentrated acids, even hydrochloric acid, dissolves in concentrated acetic acid, and shows the same four-banded absorption spectrum that it gives in acid, alcoholic, or ethereal solutions. A constant difference exists between the spectra of these solutions. In the alcoholic solution the absorption-band in the red is farther from the Fraunhofer's line D than it is in the ethereal solution. In the former the centre of the band has a wave-length of about 627; in the latter, of about 638.

This four-banded spectrum belongs, therefore, to hæmatin, and not, as Preyer maintains, to a colouring matter free from iron, the so-called hæmatoïn.

By evaporating the acid ethereal solution, yellowish-brown rhombic crystals and spindle-shaped thin tables are obtained. In a similar manner, by using sulphuric, hydrochloric, or other acid, crystals may be procured whose solubility in acids and alkalis corresponds with that of hæmatin crystals, as also do the absorption-spectra which are given by their solutions.

Although these crystals contain iron, they are in all probability identical with Preyer's *hæmatoïn-crystals* and with Lehmann's hæmatin-crystals; whilst they are closely related to if not the same as hæmin-crystals.

By the action of acids on blood, a peroxidised product has been obtained, from which the oxygen can be again extracted by strong reducing agents, with formation of oxyhæmoglobin, and subsequently of reduced hæmoglobin. This substance was called by Sorby, *Peroxyhæmoglobin*, by Hoppe-Seyler, *methæmoglobin*. It is the same substance as was described by Gamgee, under the name nitrilhæmoglobin, and may be prepared by acting upon blood with oxidising agents, such as potassium permanganate.

Peroxyhæmoglobin, in alkaline solution, has a three-banded spectrum. In acid solutions the spectrum has four absorption-bands similar to those of acid hæmatin.

The most characteristic band has a wave-length of about 633, but by addition of acid to the blood, the position of the band changes with the intensity of the acidity, being moved towards the red end of the spectrum.

The relation between hæmatin and peroxyhæmoglobin must be sought by investigating the bearing of the albumin. F. J. L.

The Elimination of Ammonium Chloride in the Urine. By LUDWIG FEDER (*Zeitschr. f. Biologie*, xiii, 256—298).—The ammonium chloride appears to undergo dissociation, the chlorine being eliminated more rapidly than the ammonia; whilst the urine contains an increased amount of urea due to an augmented decomposition of albuminoids.

These results are somewhat analogous to those which Voit found to follow the administration of sodium chloride. F. J. L.

Synthesis of Fat. By A. PEREWOZNIKOFF (*Chem. Centr.*, 1877, 22, 23).—It has hitherto been believed that the bodies formed by saponification of fat in the small intestines are absorbed by the lacteals and blood vessels. Röhrig, however, considering that the soda and potash soaps meet with lime and magnesia in the blood, and are converted into insoluble lime and magnesia-compounds, supposes that the former bodies are not found in the blood. In proof of this view, he has carefully examined the blood of dogs, and found no trace of soaps. From his researches, Röhrig is not disposed to combat the results of Radziejewsky's experiments, which proved that fatty soaps can serve as materials for the synthesis of fat. Kühne supposes that the synthesis of fat can take place in the fat-cells. Radziejewsky, however, thinks that it takes place also in the intestinal epithelium and blood corpuscles, but adduces no facts in support of his view. If the researches of Röhrig are correct, the soaps absorbed in the intestine should disappear there after being changed into other compounds. The experiments were made with dogs which were fed with albumin, glycerin, and ordinary medicinal soaps, freed from fat by means of ether. In other cases a mixture of soap and glycerin was introduced directly into the duodenum. Parallel experiments were also made with dogs unfed, fed on albumin, and on fat, and on some in which solution of soaps, without glycerin, were directly introduced into the duodenum. The conclusion is, that fats are formed in the intestinal epithelium, and possibly also in the villi (zotten), from soaps and glycerin. G. T. A.

Chemistry of Vegetable Physiology and Agriculture.

Blanching of Green Leaves in Bright Sunshine. By J. BOEHM (*Landw. Versuchs-Stat.*, xx, 463—468).—Scarlet-runner seedlings were grown in a bell jar, exposed for 14 days to the direct light of the sun in August, half the bell-jar being protected from the light by a paper screen. The primordial leaves of the plants directly exposed to the light, were dwarfed, and had only a slight green colour; whilst the plants in the shaded part of the vessel enjoyed their normal growth. On exposure to very bright sunshine, the fully-developed leaves of the scarlet runner are first bleached, then turned brown, and are finally destroyed. The under side of the leaf is much more sensitive to the action of bright sunshine than the upper side.

W. C. W.

Artificial Production of Chlorophyll in Living Plants, in the Absence of Light. By C. KRAUS (*Landw. Versuchs-Stat.*, xx, 415—421).—Experiments on barley, maize, and wheat show that chlorophyll can be artificially produced by the action of dilute methyl alcohol, or by checking the growth of the plant. A small quantity of methyl alcohol, diluted with water until the mixture possessed only a feeble alcoholic odour, is poured into a test-tube; a few germinating seeds, resting on a plug of cotton-wool, are brought into the tube a short distance above the surface of the liquid, and the mouth of the vessel is lightly closed. After remaining in a dark place for several weeks, the plants are found to have grown very slowly, and to have acquired a decided green colour, even if the roots have withered. The same results are obtained if the experiment be varied by wrapping the seeds in moist rags exposed to the vapour of dilute methyl alcohol, or by allowing the roots of young sprouts to dip into dilute wood spirit, or by exposing germinating seeds to the vapours of dilute methyl alcohol in a Nobbe's apparatus.

Some germinating seeds, supported by a plug of moist cotton-wool, are brought into a test-tube, at the bottom of which is a small quantity of water; and a second plug of wool is inserted about 2 centimeters above the first. When the plants grow, their leaves coming in contact with this plug are bent in all directions. In a few weeks those portions of the leaves which are suffering most pressure turn decidedly green in colour, but on prolonging the experiment, the green colour, instead of becoming deeper, fades away. W. C. W.

On Vegetable Glycogenesis. By V. JODIN (*Ann. Chim. Phys.* [5], xii, 491—504).—The author relates a series of facts, from which he draws the following conclusions:—

1. A great number if not all the vegetables belonging to the higher classes contain, distributed through their organisms, sugar which consists of a mixture of saccharose and inverted sugar.

2. In the same plant the average amount of sugar in the leaves is very small, but it attains its maximum in the flowers, fruits, stems, and roots, which possess the chlorophyllic function in a slight degree only.

3. The small quantity of sugar in the leaves cannot be brought forward as a proof against the direct production of sugar by these organs.

4. The constant presence of a certain quantity of sugar in fungi appears to prove that the glycogenic and chlorophyllic functions are independent of each other. L. T. O'S.

Amount of Fat in Commercial Gluten. By H. RITTHAUSEN (*Landw. Versuchs-Stat.*, xx, 408).—The author has previously shown that freshly prepared gluten contains on an average 4·5 per cent. of fat. The statement in E. Wolff's tables on the composition of fodder, that commercial gluten contains 1·5 per cent. of fat, is incorrect, and the small amount of fat found by Wolff is supposed to be due to the impossibility of completely extracting the fat from dried horny gluten by means of ether. W. C. W.

Presence of Stearic Acid in Rye Grain. By H. RITTHAUSEN (*Landw. Versuchs-Stat.*, xx, 412). In reply to the criticisms of

J. König (*Landw. Versuchs.-Stat.*, xvii, 1—15), the author remarks that he did not mean to maintain that stearic acid never occurs in rye, but that the particular samples of rye which he analysed contained neither stearin nor stearic acid. W. C. W.

Note on Rheum Officinale grown in England. By H. SENIER (*Pharm. J. Trans.* [3], viii, 444).—The root was compared with English *Rheum rhaponticum*, and with the East Indian root.

The dried powders showed a marked difference in colour; the order of brightness being (1) English officinale; (2) East Indian; (3) Rheum rhaponticum.

The infusions varied but little in colour.

	British pharmacopœia. Extract per cent.	Rectified spirit. Extract per cent.	Ash per cent.
East Indian root	45	38	12·72
Rheum rhaponticum..	29	21	7·90
English officinale	25	17	4·66

From these results it is concluded that the root of *Rheum officinale* is of less commercial value than that of *Rheum rhaponticum*.

A. J. C.

Analyses of Fodder. By H. RITTHAUSEN (*Landw. Versuchs-Stat.*, xx, 409).—The residue obtained in tallow melting is used as food for pigs, and has the following composition:—Water, 8·42; ash, 4·96; fat, 25·36. Nitrogenous matter (containing (15·609 per cent. N.), 61·26. Millet seed contains water, 11·74; ash, 3·61; fat, 4·15; albuminoïds, 10·54; fibre, starch, and carbohydrates, 69·96 per cent.

Juniper berries contain:—Water, 10·77; ash, 3·37; grape sugar, 14·36; other substances soluble in water, 11·70; fat, resin, and ethereal oil, 12·24; albuminoïds, 5·41; fibre, 31·60; non-nitrogenous matter, soluble in sulphuric acid and caustic alkalis, but not in water, 10·55 per cent. W. C. W.

Utilisation of Norwegian Fish Guano. By O. KELLNER (*Landw. Versuchs-Stat.*, xx, 423—438).—Fish guano is chiefly used as a manure, but its employment would be more general if the phosphates and nitrogenous compounds it contains were in a more soluble form. Attempts to render these bodies soluble, by treating the guano with sulphuric acid or with caustic alkalis, have been unsuccessful. Better results were obtained by allowing a mixture of the guano with gypsum, to ferment; by this means from 40 to 48 per cent. of the nitrogen could be brought into solution. Previous experiments (*Journ. für Landw.*, 1876, 265—297) have shown that the use of fish guano as food for cattle, is the most convenient mode of rendering the nitrogenous matter soluble. The following experiments prove that the value of the phosphoric acid in the guano, as a manure, is also increased by this treatment. The fish guano was used in the form of a fine meal. Its composition was—

Albuminoïds.	(N).	Fat.	Ash.
56·04	(9·44)	2·11	41·85

The two sheep which formed the subjects of these experiments, at first refused to eat the fish meal; they readily ate it, however, when mixed with groats, and finally showed a decided liking for this strange food.

The following analyses show the composition of the dried excrements of these animals; A when each sheep was fed on 656·85 grams of dry hay and 400 grams of groats per day, and B when 150 grams of fish meal were added to the above rations.

	A		B	
	No. I.	No. II.	No. I.	No. II.
Albuminoïds	10·12	9·75	10·94	10·81
Fibre	41·33	42·23	34·16	34·07
Fat	3·50	3·22	3·19	3·26
Non-nitrogenous extractive matter	34·10	33·96	31·19	31·64
Ash	10·95	10·84	20·52	20·22
Total weight of dry excrement per day	427·04	420·51	442·90	445·68

Water containing carbonic acid in solution, dissolved 18·35 per cent. of the phosphoric acid contained in fish guano, and 67·5 per cent. of the phosphoric acid in the fresh sheep dung. After the dung had been kept two months, and decomposition had set in, the solubility of the phosphoric acid rose to 73·24 per cent.

Hence the fish meal not only serves to fatten the sheep, but its value as a manure is increased by passing through the animal's alimentary canal.

W. C. W.

Schizomycetic Fermentations. By Alb. Fitz. (*Deut. Chem. Ges. Ber.*, xi, 42—55).—This is a continuation of former papers, of which abstracts have appeared in this *Journal* (1877, i, 226; ii, 214).

It was shown in the latter of these papers that the fermentation of glycerin ceases when a certain proportion of butyl alcohol has been formed in the liquid containing it. The author has since found that in some cases the fermentation has been stopped or altogether prevented by the presence of a peculiar ferment (a *schizomyces*), which reduces sulphuric acid in the sulphates present to hydrogen sulphide. This result may be prevented by using a pure ferment and boiling the liquid before adding the ferment.

The volatile acids formed in the fermentation of *mannite* are butyric, caproic, and acetic, the two latter in small quantity only. The non-volatile acids are succinic and lactic.

Starch yields, by fermentation with *schizomyces*, 35 per cent. of butyric and 9 per cent. of acetic acids, together with a small quantity of succinic acid. *Inulin* appears to yield the same products.

Lactose is readily made to ferment by *schizomyces* (but not by *sac-*

charomyces or *mucor*, as formerly believed), but yields, amongst other products, about 3 per cent. of alcohol, chiefly ethylic.

Dulcite yields a little alcohol, much volatile acid (chiefly butyric), and a trace of non-volatile acid.

Quercite yields normal butyric acid only.

Ferment-organisms.—The author has found that when a liquid containing glycerin is caused to ferment by introducing into it a little fresh cow's dung, the alcohol formed consists of about equal parts of ethyl and normal butyl alcohols; whilst the organisms developed in the liquid are two kinds of *schizomyces* (Cohn's *bacilli*), differing considerably in zize. The larger of these, distinguished as *Butyl-bacillus*, produces only normal butyl alcohol, the smaller (*Bacillus subtilis*) only ethyl alcohol. The methods of cultivating either of these organisms free from the other are fully described in the paper, which contains drawings of their appearance in the microscope. The fermentation of starch by means of *Bacillus subtilis* affords an excellent means of obtaining butyric acid. J. R.

Analytical Chemistry.

The Absorption-Spectrum of Potassium Permanganate, and its Application to Chemical Analysis. By E. BRÜCKE (*Chem. Centr.*, 1877, 139—143).—Instead of the broad absorption-bands exhibited by concentrated solutions of potassium permanganate, five separate streaks are seen when the solutions are dilute, and these may be used to indicate the presence of unchanged permanganate in coloured liquids.

Iron.—If it is desired to estimate quantitatively a relatively small amount of ferrous salt in a solution of a ferric salt, a small quantity of permanganate is added, and after this a titrated solution of the ferrous salt, till the streaks disappear; the excess of the latter solution can then be determined, and the original amount of ferrous salt calculated.

Iodine.—The turbidity produced in the reaction is no hindrance when the spectroscope is used, if the solution is sufficiently dilute. The following method is recommended. The permanganate is added till the separated iodine no longer dissolves on shaking; water is then added till the iodine dissolves, and more permanganate is added, till the reaction takes place very slowly, as is shown by the whole five streaks remaining visible for some time; the reagent is then added in excess, and the whole quantity used is read off. The liquid is covered and left in a cool dark place for an hour or two. A measured quantity of the clear stratum is then titrated, and from the value of this, together with the total volume of the liquid, the excess of permanganate is calculated. Possibly by practice the exact point might be determined at which the decomposition of the iodide ends and the oxidation of the iodine begins, and thus the quantity of free and combined iodine in a solution might be determined at one operation.

Cobalt.—The similarity of colour in cobalt compounds and potassium permanganate is no hindrance when the spectroscope is used.

G. T. A.

Detection of the Oxygen Acids of Iodine in Nitric Acid by Sulphuretted Hydrogen and Starch Solution. By E. Biltz (*Chem. Centr.*, 1877, 86).—About 3 to 5 grams of the nitric acid to be tested are diluted in a test-tube about 1·3 cm. wide, with an equal weight of water; the mixture is shaken up with a few drops of starch solution, and sulphuretted hydrogen added carefully drop by drop. The smallest trace (a thousandth part of a per cent.) of iodic acid present in the nitric acid is easily detected, as it forms a distinct blue ring in the mixture, which is rendered more clearly visible by holding the tube over a white disc. This test is more delicate than the unsafe ordinary test at present used, and the author therefore recommends its adoption in place of the latter.

D. B.

Estimation of Ammonia in the Air and in Rain-water of Montsouris. By A. Levy (*Compt. rend.*, lxxxiv, 1336).—A previous paper (*ibid.*, lxxxiv, 273) contained the results for November and December, 1876, and January, 1877; the present one contains those for February, March, and April, 1877.

From November, 1876, to April, 1877, the mean monthly amounts of ammonia contained in 100 cubic meters are the following: 1·1, 2·6, 2·8, 3·7, 4·6, and 3·9 milligrams.

The air at Montsouris contained no ammonia on the 4th, 9th, 12th, 13th, 20th, and 30th November, and the 7th December. The maximum in 100 cubic meters of air was 9 mg. on the 2nd and 17th March.

C. W. W.

Comparison of the Action of Sodium-amalgam and of Zinc as Reagents for Hager's Arsenic Test. By Al. Jandousch (*Chem. Centr.*, 1877, 101—102).—Since sodium and mercury are generally free from arsenic, E. Davy has recommended their use for the estimation of the latter substance. The sodium and mercury are used in the proportion of 1 : 8. The amalgam evolves hydrogen gas when water is added to it, but requires a small quantity of acid to give satisfactory results. It is, however, probable that by altering the proportions of sodium and mercury the addition of acid may be dispensed with.

The author uses a strip of parchment paper moistened with silver nitrate for forming the arsenic mirror. To obtain the latter in this manner a slow stream of hydrogen suffices, and the amalgam treated with water alone answers perfectly well. It is advisable to use an acidified solution of silver nitrate, as a neutral solution is apt to suffer reduction and turn the paper brown. 0·25 gram of argentic nitrate, 5 grams of water, and 2 drops of nitric acid form the solution which the author prepares. He attaches much importance to Davy's statements as to the fact that sulphides of arsenic give the same reaction when the amalgam is used. For distinguishing arsenic and antimony, Davy recommends treating the paper with ammonium sulphide and testing the sulphide formed with hydrochloric acid as usual. This test may also be used for every operation to determine whether the silver nitrate has been reduced by substances other than arsenic and antimony. D. B.

Analysis of Vanadium Sulphate and Double Sulphate (Alkaline). By B. W. GERLAND (*Deut. Chem. Ges. Ber.*, x, 1513—1516).—The author recommends the following process for the successive estimation of sulphuric acid, vanadium and the alkali-metals in the same portion of substance. To the solution of the substance in, or previously acidified with, nitric acid, lead nitrate and alcohol are added, and the solution is filtered from the precipitated lead sulphate. In presence of vanadic acid a small quantity of the latter is liable to be carried down at the same time. In this case the precipitate, which will be coloured yellow, is digested with a solution of ammonium carbonate. The lead sulphate is thereby converted into carbonate; the sulphuric acid passes into solution and is estimated after filtration. From the insoluble portion the lead carbonate is removed by boiling with dilute acetic acid, leaving the lead vanadate undissolved. It is estimated together with the main portion of the vanadic acid. The filtrate from the lead sulphate is neutralised with ammonia and acidified with acetic acid. The vanadic acid is precipitated by the addition of lead acetate in excess. If vanadium tetroxide be also present, bromine water is added until the precipitate assumes a bright yellow colour. The precipitate of lead vanadate, after filtration, is dissolved in nitric acid, and from the solution the lead is precipitated by sulphuric acid. The filtrate from this precipitate is evaporated to dryness, and the residue ignited with the usual precautions. The vanadium is thus obtained and estimated in the form of pentoxide. The alkalis are estimated in the usual way in the filtrate from the lead vanadate. In the determination of water by the usual method the author substitutes for lead oxide, sodium carbonate which has been previously heated to 300° and allowed to cool. In analysing sulphates of the lower oxides, the substance is mixed with a little potassium chlorate, in order to prevent the sublimation of sulphur.

The author also recommends, and gives the necessary details for, the volumetric estimation of vanadium by means of potassium permanganate. C. F. C.

Use of Vanadium for the Titration of Permanganate. By B. W. GERLAND (*Deut. Chem. Ges. Ber.*, x, 1516—1517).—This method, which consists in bringing a known weight of the pentoxide into solution, reducing by means of sulphurous acid, boiling to expel the excess of the latter, and titrating with the permanganate solution under trial, has been known and practised for some years. It yields excellent results. C. F. C.

A New and Ready Method for the Estimation of Nickel in Pyrrhotites and Mattes. By MARGARET S. CHENEY and ELLEN SWALLOW RICHARDS (*Amer. J. of Sci.* [3], xiv, 178—181).—This method is based upon the fact that phosphate of nickel is completely soluble, while phosphate of iron is almost insoluble, in acetic acid in the presence of an excess of sodium phosphate.

The ore is dissolved in hydrochloric acid with the addition of a little nitric acid; the solution is treated with hydrogen sulphide and filtered, the filtrate boiled, the iron oxidised with nitric acid, and ammonia is added until a permanent precipitate begins to form. Acetic acid is then added until the precipitate is redissolved. To this boiling hot solution a hot concentrated solution of ordinary sodium phosphate is added in excess, and the nearly white precipitate is filtered off and washed with hot water containing acetic acid. The filtrate is heated nearly to boiling, and caustic potash added until the odour of ammonia is distinctly perceptible. The apple-green precipitate of nickel phosphate is partially washed and dissolved in a little dilute sulphuric acid; the solution rendered strongly alkaline by ammoniahydrate; and the nickel precipitated by the battery. If more than 3 per cent. of nickel is present, the precipitate of phosphate of iron must be redissolved and treated as before, as it may contain a little nickel.

This method saves much time, and enables the separation of the nickel to be effected with much more concentrated solutions. The precipitation of the nickel by electrolysis also takes place more easily from a solution of the phosphate.

The results of various analyses are given, showing that the method yields tolerable results. F. D. B.

Direct Estimation of Gold in Antimony-regulus in presence of Arsenic, Copper, Iron, and Zinc. By A. GAWALOWSKI (*Chem. Centr.*, 1877, 651).—100 grams of the powdered regulus are melted with zinc free from gold in a capacious porcelain crucible; the melt is poured on to a porcelain plate; and the alloy is broken in pieces, and dissolved in dilute sulphuric acid, first cold and afterwards heated. The antimonetted hydrogen, which sometimes contains arsenetted hydrogen, is passed into a solution of silver nitrate, in order to test for arsenic, if required. After cessation of effervescence, the residue is boiled, allowed to cool, again stirred up with warm water, and filtered as long as salts go into solution. In this manner copper, iron, and zinc are completely removed. The residue is dissolved in *aqua regia*, and evaporated to dryness; it is then treated with alcohol and decanted till the alcohol is no longer coloured yellow; and the alcoholic extract is evaporated and treated with ether. The ethereal solution is evaporated in a tared porcelain crucible, and the gold weighed as metal. This method gives results which agree well with one another; it is also applicable to antimony ores. They are roasted, dissolved in hydrochloric acid, and the metals are precipitated with zinc. The rest of the process is as before. W. R.

Estimation of Alkalis in the Ash of Plants. By R. HORNBERGER (*Landw. Versuchs-Stat.*, xx, 457—462).—In estimating the alkalis in the ash of plants, after precipitating the sulphates with barium chloride and adding ammonia, it is advisable to filter before adding ammonium carbonate and oxalate, since ammonium carbonate acts on calcium phosphate, forming ammonium phosphate and calcium carbonate. If this precaution be neglected, a small quantity of phosphoric acid will frequently be mixed with the chlorides of potassium and sodium W. C. W.

Volumetric Estimation of Alcohol. By T. T. MONELL (*Chem. Centr.*, 1877, 24—25).—The addition of a salt of cobalt to an alcoholic solution of ammonium thiocyanate produces a deep blue colour, which disappears on addition of water, and reappears on further addition of alcohol. If a measured quantity of this dark blue liquid is poured into a cylinder, and the liquid to be tested is added, till the colour becomes that of a strip of pale blue glass, the volume of the mixed liquids will be greater in proportion as the specimen was richer in alcohol. These volumes once fixed would always remain the same, and the percentages might be marked on the cylinder, and directly read off. The blue liquid must always be prepared with alcohol of the same strength, and the same strip of blue glass must be used. The nitrate is the best cobalt salt for the purpose. In the case of coloured brandies the colour obtained is green, instead of blue, and therefore two cylinders must be used, one for dilution, and one for producing the same colour in comparison with the strip of blue glass. The cobalt solution may be neutral, or faintly acid, and should contain as little water as possible. The quantity of alcohol in a mixture may be estimated by this method to $\frac{1}{4}$ per cent. G. T. A.

A New Method for the Gravimetric Estimation of Glucose and of Mercury. By H. HAGER (*Chem. Centr.*, 1877, 729—730).—This process consists in the reduction by glucose, of mercuric acetate in presence of sodium chloride and free acetic acid, to mercurous chloride. The reagent is prepared by triturating 30 grams of red mercuric oxide with 30 grams of sodium acetate, adding 25 grams of glacial, or 100 cub. cent. of commercial acetic acid, and 50 grams of sodium chloride. The liquid is diluted to 1 litre. It is quite stable when kept in stoppered bottles, and out of direct sunshine. Excess of this reagent is added to the solution of glucose, and the liquid is boiled for one or two hours. Two molecules (= 360) of glucose require 18 molecules (= 1944) of mercuric oxide, and yield 9 molecules (= 2119·5) of mercurous chloride. For every 1 gram of glucose, more than 180 cub. cent. of reagent must be added. The solution is not acted on by saccharose, glycerin, gum-arabic, dextrin, or uric acid, but is reduced by some of the constituents of urine. The weight of the calomel divided by 5·88, gives the amount of glucose, and divided by 6·19, its equivalent in saccharose. W. R.

Estimation of Dextrose, with Special Reference to the Method of R. Sachsse.—By F. STROHMER and A. KLAUS (*Chem. Centr.*, 1877, 697—703, and 713—720).—Sachsse's reagent is prepared as follows :—18 grams of pure dry mercuric iodide is dissolved in water, with addition of 25 grams of potassium iodide. To this solution 80 grams of potassium hydroxide in solution are added, and the liquid is diluted till it occupies 1 litre; 40 cub. cent. of this solution are boiled in a basin, and the sugar solution, containing about 0·5 per cent. of sugar, is added, till all the mercury is precipitated; the end-point is indicated by stannous chloride ceasing to give a precipitate, when added to a drop of the solution. The authors have compared this process with Fehling's method, and have arrived at the following conclusions:—

1. Sachsse's process is correct, if applied to the determination of dextrose in solutions of pure dextrose, and has this advantage over Fehling's method, that the end-point is much more easily recognised.

2. In estimating dextrose in presence of saccharose with Fehling's solution, the estimation is more nearly correct, as the quantity of the latter sugar is less: for in presence of dextrose, cane sugar is decomposed to a greater extent by Fehling's solution than when no dextrose is present.

3. For this last-mentioned estimation, Sachsse's method is quite inapplicable.

4. But it may be used for determining inverted sugar in pure solutions.

In analysing the mixture of sugars obtained from starch, Fehling's method has been almost exclusively employed. The authors corroborate Heinzerling and Rumpff's statement, that Fehling's solution is without material action on erythro- and achro-dextrin, which are the constituents of commercial dextrin. It is accordingly possible to estimate dextrose in presence of dextrin. Sachsse's process cannot, however, be used for this purpose, as the mercury is precipitated when the solution is boiled with dextrin; it is, therefore, of use only for the determination of dextrose and inverted sugar in pure solutions of these bodies. W. R.

Estimation of Salicylic Acid. By H. HAGER (*Chem. Centr.*, 1877, 117—118).—The behaviour of pure concentrated sulphuric acid to salicylic acid seems to afford a more delicate test for the latter than any method hitherto known. By agitating the two acids together, perfectly colourless solutions should be obtained, if the salicylic acid is pure. Various samples, recognised as pure by Kolbe's method, gave yellowish to yellowish-brown solutions when treated in the manner above mentioned. D. B.

Detection of Salicylic Acid in Wines and in Urine. By E. ROBINET (*Compt. rend.*, lxxxiv, 1321).—Take 100 c. c. of the wine, precipitate with lead acetate, filter, add sulphuric acid to precipitate the lead, filter again. To the perfectly clear liquid add a few drops of ferric chloride, which, if there is the smallest trace of salicylic acid in the wine, will produce a fine violet colour. The presence of 2 or 3 milligrams of salicylic acid in a litre of wine can thus be shown. The method of proceeding in the case of urine is the same, and the indications are even more delicate. Care must be taken to have an excess of sulphuric acid in the liquid. C. W. W.

On a Method of Determining the amount of Protein Compounds in Vegetable Substances. By J. A. WANKLYN and W. J.

COOPER (*Phil. Mag.* [5], iii, 382—385).—The determination of the amount of protein compounds in vegetable food is important, since the animal derives such compounds from its different kinds of vegetable food. The estimation of nitrogen in the food has hitherto formed the basis for calculating the percentage of protein. The Will-and-Varrentrapp method, when applied to food, gives an incorrect result, and Dumas' method yields a correct result only when extraordinary precautions are adopted. The ammonia-process is recommended by the authors, who adapt it as follows:—One gram of the food is accurately weighed, mixed with 20 c.c. of decinormal caustic potash solution, then made up to a litre with water, and the whole mixed by shaking. From 10 to 20 c.c. of this mixture (= 10 or 20 mgr. of substance) are introduced into a retort in which a mixture of 300 or 500 c.c. of good drinking-water with 50 c.c. of a solution containing 10 grams of potash and 0·4 gram of potassium permanganate has been distilled until no more ammonia appears in the distillate. The distillation is then proceeded with, and the ammonia produced from the protein compounds is determined in the distillate by the Nessler-test. The weight of ammonia found, when multiplied by 10, gives a fair approximation to the actual quantity of vegetable protein. Wheaten flour from different sources was found to contain from 10·0 to 11·3 per cent. of protein; maize, oats, and barley closely resemble wheaten flour in this respect; rye yielded 14·5 per cent., whilst pea-flour seems to contain as much as 23 per cent. of protein; rice yielded only 6·2 per cent., about half as much as wheaten flour. F. C.

On the present Methods for Analysing Milk, with special reference to Cow's and Human Milk. By G. CHRISTENN (*Landw. Versuchs-Stat.*, xx, 439—455).—The author discusses the relative merits of several methods for analysing milk, viz., that of Haidlen (*Watts's Dict.—Ann. Chem. Pharm.*, xlv, 273), Hoppe-Seyler (*Phys. Path. Chem. Anal.*, 434), Tolmatscheff (*Hoppe-Seyler's Med. Chem. Untersuch*, 273), and Brunner (*Pflüger's Archiv. f. Physiol.*, vii, 422), also of Schukoffsky's method for the determination of the fat in milk, and arrives at the conclusion that a slight modification of Haidlen's process is the best, as it yields good results, and can be used, not only for the analysis of cow's and human milk, but also for that of any animal. The process consists in mixing the milk with one-fifth of its weight of finely powdered gypsum, evaporating to dryness at 110°, and weighing the residue, the loss giving the amount of water, and the weight of the residue, *minus* the gypsum, giving the weight of solid constituents. The fat is then extracted from this residue by ether, then the milk-sugar and soluble salts by alcohol of 85 per cent. The last residue contains the albuminoïds and insoluble salts, the weight of which is equal to that of this residue after deduction of the gypsum. The quantities of the soluble and insoluble salts are determined in the usual manner, and the weight of the latter deducted from that of the last residue gives the amount of the albuminoïds.

The alterations in this method, proposed by Christenn, are—1st, to add powdered glass instead of plaster of Paris to the milk before evaporating to dryness, in order to avoid errors arising from the hygroscopic nature of the plaster of Paris, and from the solubility of this substance in dilute alcohol. This latter source of error gives too high results for the sugar, at the expense of the albuminoïds.

2ndly. To dry the residue at 95—100° instead of 110°.

Good results are also obtained by Hoppe-Seyler's process, and by Schukoffsky's method for the determination of fat in milk. In Tolmatscheff's process a portion of the albuminoïds precipitated by alcohol is dissolved by washing with dilute alcohol. Brunner's mode of analysis is difficult to carry out, the albuminoïds are always too low, and the results are not trustworthy.

Brunner's statement that woman's milk contains from 2·3 to 4·5 times more nitrogen than is present as albuminoïds, is incorrect, and no doubt results from the errors inherent in his method. All the nitrogen in cow's and woman's milk is present as albuminoïds. The composition of woman's milk is incorrectly given by Brunner, as a comparison with the mean of several analyses shows:—

	Brunner.	
Total solids	—	12·75
Water....................	90·00	87·24
Fat......................	1·73	4·23
Sugar....................	6·23	5·96
Albuminoïds	0·63	1·90
Soluble salts	1·41	salts 0·28

The following process, invented by the author, gives satisfactory results, closely agreeing with those obtained by Haidlen's method. 10 grams of milk are mixed with 10 c.c. of ether and 20 c.c. of alcohol; the mixture is well stirred; and the precipitated albuminoïds are collected on a weighed filter, and washed with a mixture of 1 part of ether and 2 of alcohol, until the filtrate, which is at first turbid, begins to run through clear. The precipitate, dried at 95—100°, gives the weight of albuminoïds and insoluble salts; by ignition the weight of the latter is obtained. The filtrate evaporated to dryness gives the amount of fat, soluble salts, and milk-sugar; the fat is extracted with ether, the residue weighed, and the fat determined by difference. The mixture of soluble salts and sugar is ignited, and the residue treated with hot water. The weight of soluble salts is obtained by evaporating the aqueous solution to dryness and igniting.

Abstractor's Note.—Christenn appears to be ignorant of Wanklyn's observation, that milk residue can be completely dried without the addition of any solid matter. W. C. W.

On Fats used for the Adulteration of Butter. By C. HUSSON (*Ann. Chim. Phys.* [5], xii, 469—480).—This paper describes the characters exhibited by pure butter and by butter adulterated with margarin, lard, and suet: (*a*.) When dissolved with aid of heat in castor-oil. (*b*.) When fused with glycerin, the emulsion thus produced being heated with a mixture of alcohol and ether, and then left at rest. The microscopic characters of the flocculent deposits formed in the latter case are also described and illustrated by engravings.

L. T. O'S.

Testing of Lubricating Oils. (*Dingl. polyt. J.*, ccxxvi, 307—309.) —A good oil unmixed with resin can be distinguished from an adulterated or impure oil by placing it on a glass-plate out of the action of dust, &c. The pure oil remains of a fatty nature for as long as six months, while in the other case the resin sets as a kind of glaze. A pure mineral oil will not freeze at −15°, and this is important in the case of machinery exposed to the weather.

Wiederhold (*Wochenschrift des Vereines Deutscher Ingenieure*) proposes to test the presence of acids (fatty or resinous) by adding suboxide of copper; a green coloration shows the presence of acids, and thus determines the presence of impurities.

G. Merz (*Deutsche Industriezeitung*, 1877, pp. 124 and 135) places 2·5 c.c. of oil with 5 to 10 times its volume of spirit of wine of 90 per cent. in a glass flask provided with a glass stopper, and adds a little turmeric-infusion. He then adds soda of known strength, and shakes up until the liquid changes from lemon-yellow to reddish-yellow. The addition of ether to the alcohol renders the reaction more certain. A method recommended for choosing mineral oils for lubricating machinery is the following:—A small pot is taken in which water can be boiled, and over this is placed a sheet of zinc which has been cleaned with emery-paper. A drop of oil is let fall on this zinc plate, and the pot boiled for about 1½ hours. The plate is then removed, allowed to cool, and the oil examined. Good oil of 3·5° of acidity leaves the zinc unchanged. Oil of 15° to 20° acidity remains bright, but the zinc loses its brightness and is covered with a thin, dark, almost black dust. Oil of greater acidity, to 30° or 60°, covers itself with a skin, and lies on the zinc as an opaque, white, thick, pasty mass. The oils between the varieties named give characteristic results. A sheet of lead gives better results, but does not so easily yield a clean, smooth surface. S.

Technical Chemistry.

Warming with Hot Air. By R. KAYSER (*Chem. Centr.*, 1877, 126, 127).—An apparatus for heating purposes must be examined in two different aspects; first, with regard to its heating effect, and secondly with regard to its influence on the composition of the heated air. The latter point has been fully investigated by the author in the case of a hot-air apparatus, with the following results:—

1. *Investigation as to the presence of Carbonic Oxide.*—The author used Ludwig's method based on the conversion of carbonic oxide into carbonic acid by oxidation with chromic acid. The heated air was invariably found to contain carbonic oxide, whereas the air, before entering into the heating apparatus, was quite free from that gas.

2. *Investigation as to Decomposition-products of Dust.*—On passing the hot air through absolute alcohol, the latter assumed a yellow to yellowish-brown colour. After evaporation, an extract was obtained

insoluble in water, having an acrid taste and an empyreumatic smell. The air, before entering the heating apparatus, was heated in a similar manner, but negative results were obtained.

The peculiar feeling of dryness in the throat which is experienced on breathing air thus heated, is very probably due to this acrid tarry substance, which appears to be formed by the partial combustion of the organic constituents of the dust, in contact with the heated surface of the stove or pipes. The presence of carbonic oxide in the heated air may be explained in a similar manner; or this gas may pass into the air of the apartment from the hot air of the stove itself, in consequence of the power which it is known to possess of penetrating red-hot iron. D. B.

Sulphurous Acid Ice-Machine. By R. PICTET (*Chem. Centr.*, 1877, 81).—The refrigerator used is liquid sulphurous acid; it is easily and cheaply prepared, and exerts at − 10°, a pressure of rather more than one atmosphere, and at + 35° not more than four atmospheres. Two tubular boilers are used, one serving for evaporation, the other for condensation. The former is exhausted by an air-pump, the vapours formed being compressed in the second boiler. A narrow tube, fitted with a tap, conducts the condensed liquid from the second boiler to the first. Salt water passes through the tubes of the first boiler, and serves to convey the cold to the proper freezing vessels; while water passes through the tubes of the second boiler, and is used for cooling purposes. The acid used does not attack the metallic portions of the apparatus, nor does it dissolve the fat used as lubricant; while it serves as lubricator for the piston of the pump. The above apparatus is said to produce 1,000 kilos of ice at a price of 10 francs.

D. B.

Red Coloration of Yellow Tiles. By RUD. BIEDERMANN and S. GABRIEL (*Deut. Chem. Ges. Ber.*, x, 1548—1551).—The authors have investigated the cause of the occurrence of the bright-red patches in yellow tiles, which are a source of much inconvenience to the makers. Their analyses prove that this is referable, immediately, to an excess of 10 per cent. sulphuric acid present in the red portions, over that contained in the yellow, and not to different states of oxidation of the iron present in either. The sulphuric acid exists in combination as calcium sulphate, the latter resulting from the decomposition of the iron-calcium silicates, which form the basis of the tiles.

The removal of calcium from this compound brings into play the red-colouring property of ferric oxide, or rather silicate. The formation of calcium sulphate is ascribed by the authors to the sulphur contained in the coal which is employed in burning the tiles. This explanation is based upon the authors' direct observation that calcium sulphate is formed by passing moist sulphurous acid gas, together with air, over lime kept at a red-heat. C. F. C.

A New Process for the Electrical Deposition of Metals, and for constructing Metal-covered Glass Specula. By A. W. WRIGHT (*Amer. J. of Sci.* [3], xiv, 169—178).—In a previous paper

(*Amer. J. of Sci.*, January, 1877) an account was given of a method of producing metallic films upon the inner surface of exhausted glass tubes by the action of a series of energetic electrical discharges. The apparatus has now been modified so as to render it possible to deposit the films on pieces of plane glass. This is done by hanging the piece of glass in an exhausted glass globe about 7 centimeters in diameter, so that it lies horizontally about 3 millimeters below the metal electrode. By slightly inclining the globe, the various portions of the glass plate can be brought opposite the electrode, thus enabling the operator to obtain a film of equal thickness over the entire plate. Before making an experiment, the glass globe was exhausted, and dry hydrogen afterwards admitted; this process was repeated two or three times, and finally the globe was exhausted by means of the Sprengel pump. The use of hydrogen is not in all cases necessary, as some of the metals, especially gold, can be deposited perfectly well with only air in the receiver. The electrical apparatus employed consisted of an induction coil capable of giving sparks four to five centimeters in length, a battery of from three to six pint Grove cells, and a plunge battery of five cells. It was found advisable in most cases to regulate the strength of the current, so that the temperature of the electrode was slightly below that of a red heat.

The metallic films thus obtained have such remarkably brilliant surfaces, that they may be compared to that of clean mercury; they are, therefore, eminently adapted for specula. With this particular object in view, experiments were made which showed that the thickness of a film of gold or platinum need not be greater than 0·00018 millim., in order almost entirely to prevent the transmission of light. It is therefore evident that the figure of a perfectly wrought glass mirror will not be changed when the metal is deposited with tolerable uniformity. Moreover, a platinum film having a thickness one-fifth of the above, forms a brilliant mirror, and transmits but little light.

Platinum appears to be the best metal for those purposes. Silver is deposited much more rapidly, but unless care is taken, it is frequently deposited as a powder having a dull yellow surface; indeed, none of the silver films obtained were free from this coloration, which appears to be due to the transmission of a certain amount of the blue rays, and the consequent predominance of the complementary colour in the reflected light. The fact that a film of platinum of a certain thickness transmits orange-coloured rays, suggested the possibility of obtaining a mirror which should be perfectly white by reflected light, by depositing, first, a thin stratum of silver, and over this another of platinum, the relative thickness of the two being properly regulated by observing the colour of the transmitted light. The result was very successful, the surface being perfectly white, and the film, when observed by transmitted light, having no perceptible colour.

The surfaces obtained with bismuth were good, but not so brilliant as those of platinum. Iron deposited in this manner adheres to the glass with great tenacity, and, from a chemical point of view, is almost inert, remaining unaltered for months in contact with the air, and yielding only with difficulty to the action of nitric and nitrohydrochloric acids.

These films can be deposited on conducting materials with as much facility as upon glass. F. D. B.

On Homogeneous Iron and the Degree of Homogeneity to be expected in Iron produced by various systems of Puddling and subsequent Working.—(*Engineer*, May 11th, 1877.)—The term "homogeneous" seems to have been first applied some 20 years ago to a comparatively pure iron containing less carbon than steel, in fact, possessing none of the characteristics of the latter.

This term has been supplanted within the last ten years by the term "steel," steel meaning something better than iron. There appears, too, to be a tendency to apply the term homogeneous to puddled iron, whereas the latter is not truly homogeneous. The application of the term steel has created a false idea as to the hardness of this metal, and the cost of working it. The fracture it presents finds little favour with engineers, and its requiring much heat and power for working it has prejudiced those who have to expend their labour on it.

The author endeavours in this article to show what homogeneous iron is, and the degree of homogeneity that can be produced in different puddling furnaces. Homogeneous iron may be defined as iron with the

Tests of Hoop Iron and Steel (Pearson and Knowles' Coal and Iron Co., Crown W.I.W., Warrington). Hoops 1 *in.* × 18 *w.g.*

Steel.			Iron.		
No.	Breaking weight.	Elongation.	No.	Breaking weight.	Elongation.
	lb.	per cent.		lb.	per cent.
1	4,360	11·50	1	2,660	9·00
2	3,800	13·25	2	2,420	4·50
3	4,275	13·00	3	2,525	9·25
4	4,100	13·50	4	2,400	1·25
5	4,100	11·00	5	2,480	4·00
6	4,200	9·50	6	2,000	3·00
7	3,700	12·00	7	2,300	2·50
8	4,445	10·50	8	2,000	4·00
9	3,680	14·25	9	2,490	9·25
10	4,430	8·75	10	2,300	3·50
11	3,800	15·00	11	2,790	9·75
12	4,300	10·50	12	2,200	2·00
13	4,000	11·75	13	2,400	7·50
14	4,750	12·25	14	2,210	3·00
15	4,200	13·00	15	2,870	8·00
16	3,700	9·50	16	2,400	3·25
17	3,720	14·75	17	2,650	3·50
18	3,815	15·00	18	2,500	9·75
19	3,770	10·25	19	2,400	1·50
20	3,760	12·50	20	2,375	4·50
Average ...	4,042	12·08	Average ...	2,388	5·15

same structure throughout. Thus elements which combine chemically with it, as silicon, phosphorus, carbon, &c., do not affect its homogeneity, but slag and cinder do, as they do not unite with the iron. Iron melted and cast into ingots and then carefully heated and well worked may be called homogeneous iron. Such iron has no right to the term steel, when the carbon is not above 0·30 per cent. Homogeneous iron—or mild steel—is remarkable for its high degree of strength and ductility, as can be seen by the preceding table (p. 253).

On the face of it the steel looks twice as good as the iron; but if we obtain the comparative value for work by Mallet's coefficient, half the breaking strain has to be multiplied by the elongation per foot, when it is seen that the steel has four times the value of the iron. The following table gives experiments on Fagersta steel by Kirkaldy:—

Size of Bars.	Specimens turned to		Stress ultimate per sq. in.	Contraction of area of fracture.	Ultimate extension.	Appearance of fracture.
	Dia.	Area.				
in.	in.	sq. in.	lb.	per cent.	per cent.	
½ sq.	0·357	0·100	60,780	72·0	22·20	all silky
1 „	0·619	0·300	54,560	69·7	27·80	do.
1½ „	1·009	0·800	57,960	56·0	27·30	do.
2 „	1·382	1·500	57,453	51·8	28·60	95 per cent. silky
2½ „	1·694	2·250	57,345	31·4	20·20	all granular
3 „	1·994	3·000	52,962	57·8	31·1	all silky
		Average	56,843	56·45	26·2	

The author then goes on to describe the process of puddling, and shows that bad pig iron can produce a puddled iron with good fibre but wanting in body. This iron contains too little carbon to be strong, the silicon and phosphorus present assisting the "boiling," during which the carbon is eliminated. When but a small proportion of silicon and phosphorus is present, there is generally much carbon, and the iron breaks with a crystalline fracture, after being nicked and subjected to a smart blow. The quality of this iron becomes better the more it is worked. Iron more impure, and rendered fibrous by contained slag, is apt to become weak when overheated.

The writer noticed these facts for a long time, but the value of homogeneous iron from puddling was brought strongly before his notice only during some experiments made on iron from different ores. The heats were all of full weight and no extra precautions were taken. The puddled blooms were rolled into bars without re-heating. The annexed table gives the tests of 4 bars of Marron iron of various shapes and sizes. The ultimate strength varies from 24 to 27·3 tons per sq. in.; the contraction of area from 40 to 52·4 per cent.; the extension taken over a length of 10 in., from 22·1 in., the smallest size, to 24·2 in., the largest.

Bars 10 *in. long* (*3rd July*, 1876).

Size of Bars.	Original area.	Ultimate stress per sq. in. of original area.		Contraction of area at fracture.	Stress per sq. in. of fractured area.	Ultimate extension.	Appearance of fracture.
in.	sq. in.	lb.	tons.	per cent.	lb.	per cent.	
9/16 dia.	0·255	61,282	27·3	40·3	102,809	22·1	Fibrous
9/16 sq.	0·331	55,791	24·8	42·9	97,709	23·0	do.
3/4 ,,	0·570	54,894	24·5	40·0	91,491	24·2	do.
1/2 ,,	0·265	53,603	24·0	52·4	112,738	22·9	do.

In the following table by Kirkaldy (24th July, 1876), the first four samples represent two puddled bars of the same heat; one piece was taken from the end, and the other from the middle of each finished bar:—

Bars 10 *in. long.*

ia. of Bars.		Original area.	Ultimate strength per sq. in. of original area.			Contraction of area at fracture.		Stress per sq. in. of fractured area.	Ultimate extension.		Appearance of fracture.
in.		sq. in.	lb.	lb.	tons.	per cent.		lb.	per cent.		
dia.	M	0·963	60,351	59,584	26·6	32·8	37·1	94,786	22·7	23·3	Fibrous
,,	E	do.	58,817			41·4			24		
,,	E	0·785	54,203	54,114	24·1	46·7	46·7	101,625	26·1	26·1	do.
,,	M	do.	54,025			46·7			26·2		
,,	M	0·968	52,747	52,564	23·5	44·1	44·7	95,191	26·5	25·8	do.
,,	E	do.	52,381			45·4			25·2		

M = middle of bar. E = end.

The table on page 256, and the last 5 items on the one following it, give the results of the most important trial of all, because they represent the whole of a puddled heat, both in tests and analyses. An effort was made in this heat to get less carbon than usual, the result being 0·131 per cent., but the phosphorus and silicon increased to 0·243 per cent. on the whole heat.

	Carbon, per cent.	Silicon and phosphorus, per cent.
W.R. 3 contained....	0·180	0·093
W.T.W. contained ..	0·150	0·260
W. 5 contained......	0·115	0·310
WR. 5 ,, ...	0·090	0·345

W. S. is here omitted, as the slag was extruded, and in analyses of iron much of the phosphorus really belongs to the slag. The author thinks, too, that the last traces of carbon are removed from the iron at the expense of the oxygen of the rich slag containing phosphorus and silicon, both these ingredients being, therefore, set free to enter the iron.

Tests of Marron Iron Bars by D. Kirkaldy, 3rd May, 1876. *Bars* 10 *in.*

Description of Iron.		Original area.	Ultimate stress per sq. in. of original area.			Contraction of area at fracture.		Stress per sq. in. of fractured area.	Ultimate extension.		Appearance of fracture.
		sq. in.	lb.	lb.	tons.	per cent.		lb.	per cent.		
WS	M	0·442	56,515	55,803	24·9	42·3	40·9	94,501	24·1	23·3	Fibrous
do.	M	do.	56,470			40·2			22·6		do.
do.	E	do.	54,423			40·2			23·1		do.
WTW	M	do.	55,791	55,689	24·8	46·1	41·3	94,916	24·1	23·0	do.
do.	M	do.	55,723			46·1			23·8		do.
do.	E	do.	55,554			31·6			21·1		do.
W 5	M	do.	55,780	55,048	24·6	42·3	41·6	94,308	23·9	22·1	do. 5 p.c. crystalline
do.	E	do.	55,361			40·2			20·1		fibrous
do.	M	do.	54,004			42·3			22·3		do.
WR 5	M	do.	55,226	54,747	24·5	46·1	40·8	92,595	24·8	23·2	do.
do.	E	do.	55,181			38·2			22·6		do. peculiar
do.	M	do.	53,834			38·2			22·3		do. do.
WR 3	M	do.	52,138	51,728	23·1	50·0	50·0	103,457	25·9	25·8	fibrous
do.	M	do.	51,961			50·0			26·0		do.
do.	E	do.	51,085			50·0			25·5		do.

Chemical Analysis of Iron used in the above Experiments.

Description.	Iron.	Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.	Total.
a	99·533	0·165	0·067	0·011	0·075	Trace.	99·851
b	99·530	0·190	0·074	0·010	0·091		99·895
—	99·533	0·170	0·047	0·011	0·045		99·806
WS	99·498	0·120	0·116	0·015	0·091		99·840
WTW	99·326	0·150	0·128	0·012	0·132		99·748
W 5	99·500	0·115	0·149	0·011	0·161		99·936
WR 5	90·498	0·090	0·163	0·022	0·182		99·955
WR 3	99·704	0·180	0·019	0·014	0·074		99·991

From Tables III to VI we get the following interesting results. The cohesive power of an iron bar is the breaking weight referred to the reduced area of fracture.

Carbon. per cent.	Breaking strain. lb.	Original area.
0.090	92,595	0·442
0·115	94,308	0·442
0.120	94,501	0·442
0·150	94,916	0·442
0·165	102,809	0·255
0·170	101,626	0·785
0·180	103,457	0·442
0·190	112,738	0·265

From this it may be seen that the strength of an iron increases with the amount of carbon.

The author then goes on to describe the different puddling processes. He cites the Lowmoor as the best homogeneous iron produced. The best material is used; the best workmen employed, and these latter are carefully superintended.

The Casson-Dormy furnace gives a strong granular iron. A heat of 10 cwt. is puddled in 80 minutes from charging to withdrawal of the last ball.

The Maudslay furnace.—The form of furnace revolving on a horizontal axis appears to give the greatest promise of success in the future. When the charge is run in liquid, the working can be performed better than in former cases, but as soon as it becomes pasty and the puddler cannot get at it, the advantage is in a measure lost.

Danks' furnace.—No published reports favourable to homogeneity.

Spencer furnace gives better results than the Danks'.

Crampton furnace gives the best promise of a successful result in this direction. S.

Homogeneous Iron. (*Dingl. polyt. J.*, ccxxvi, 394—398).—Bergrath Anton. R. von Kerpely has published in the *Zeit. des Berg. und Hüttenmännischen Vereines für Steiermark*, 1877, an account of his microscopic investigations into the physical nature of iron, which support the views of Kirk, noticed above. The different kinds of iron and steel have, at the extreme ends, soft iron and spiegeleisen, one fibrous, the other largely crystalline. Soft iron shows under the microscope that the fibres are composed of three-cornered leaves joined by their edges, and that between these bundles of leaves there are spaces filled with slag. In the bloom from which the soft smith-iron is made are formed, after the shingling, crystals of octoheral and hexahedral forms. The space between the crystals contains slag as before. From this it will be seen that in the process of rolling the crystals become pressed out into thin leaves. A number of chemical analyses, with experiments on the strength of the material and a microscopic examination of the iron, have shown that, as the amount of carbon decreases, the crystals are more easily extended by pressure, and thus the stretching and bending power of the iron increases, but at the same time the thickness of the laminæ (Blättchen) and the strength of the iron decreases. If the amount of carbon remains unaltered, the strength of the iron increases by repeated heatings and rollings, as the slag becomes pressed and the laminæ or extended crystals are forced into closer union. If the carbon is present in large quantities, the crystals refuse to spread into thin leaves, but break into a number of rough, irregular fragments when rolled. These small fragments become so pressed together, if the slag be extended, that the result is a good iron. It the amount of carbon rises above 1 per cent., the fragments are too large and the iron cannot be worked in the fire.

Sulphur, copper, and silicon hinder the spreading out of the crystals into leaves under pressure, and also the movement of the fragments of crystals one over the other, especially at a red heat. If pressure be applied to overcome the resistance offered by the presence of these substances cracks and breakages occur. This is the cause of red shortness (Rothbruch).

When iron is raised to a white heat the crystalline-leaves become separated (Auflockerung), gas and air being absorbed. Such iron has a laminated structure, and is called "burnt." The air and gas can be extruded by repeated heatings and pressure. By repeated blows and hammerings the iron becomes cold-short.

The author shows that in the hardening of steel the carbon is compelled by the rapid cooling to remain in chemical union with the iron, and the homogeneous result is therefore better than slowly-cooled steel.

The author thinks that the above considerations support the idea that iron rich in carbon and with a fine crystalline structure—the so-called homogeneous iron—is to be preferred to fibrous iron. S.

Production of Potassium Ferrocyanide from Ammonium Thiocyanate. By BRUNO ALANDER (*Dingl. polyt. J.*, ccxxvi, 318).—The author has succeeded in using this bye-product in the manufacture of gas for the production of potassium ferrocyanide.

The thiocyanate is mixed with a double equivalent of potashes, coal, and iron-filings; the whole is then mixed up with oil and heated in a crucible to a red heat. The operation is over when the flame disappears from the surface. On cooling fresh precipitated hydrate of iron is added, and then the soluble matter is extracted by water, 40 per cent. to 50 per cent. of the thiocyanate is thus converted into ferrocyanide. S.

Spontaneous Combustion of Oily Wool-waste, &c. By J. J. COLEMAN (*Chem. Centr.*, 1877, 319—320).—The author has investigated the inflammability of various kinds of fibrous waste when saturated with oils, by a method which consisted in maintaining the oily waste at a constant temperature (82° C.) in a steam-chest, and observing the times which elapsed before combustion set in, and also the temperature of the mass at the moment. The results of the investigation are set forth on the next page—

	Entered into combustion after a lapse of—	At a temperature of—
Cotton waste, saturated with whale oil	3 hours.	165° C.
„ „ olive oil	4 „	177° „
„ olive oil and 20 p. c. mineral oil....................	8 „	177° „
„ olive and mineral oils in equal parts.	Unchanged after lapse of 26 hours. After 12 hours, temp. = 95° C.	
Wool waste, saturated with seal oil	3 hours.	194°
„ „ whale oil	3 „	188°
„ „ cotton seed oil	5 „	178°
„ „ olive oil	7 „	177°
„ „ refined rape oil	6 „	177°
„ „ crude „	8 „	163°
„ „ cotton-seed oil, with 20 p. c. mineral oil, seal and mineral oil, equal parts	Unaltered after lapse of 26 hours.	
„ „ olive and mineral oils, equal parts....................		
Jute waste, saturated with whale oil	8 hours	180° C.
„ „ whale and mineral oils, equal parts	Unchanged after lapse of 26 hours.	

C. F. C.

The Influence of the Constituents of Waters on Tanning.

By W. Eitner (*Dingl. polyt. J.*, ccxxvi, 524—526).—The action of ozone is doubtful. Large quantities of organic matters are always found in water containing leather in a state of decomposition. If the temperature exceeds 12°, the decomposition is increased. Eitner took solutions of calcium carbonate, magnesium carbonate, calcium sulphate, magnesium sulphate, and magnesium chloride respectively, of such strengths that each showed 20° hardness (*Dingl.*, ccx, 300), also sodium chloride solution, and water containing carbonic anhydride. Strips were cut from a hide from which the hair had been removed. These were treated with salicylic acid solution to destroy any organisms, and washed with distilled water. After four days the pieces in the sodium chloride and magnesium chloride were not at all raised; very little more in distilled water; moderately raised in the calcium and magnesium bicarbonate baths; well raised in the carbonic acid bath, and best of all in the magnesium sulphate bath. In all cases the temperature was 8° C. Increased temperature seems to favour putrefaction only.

The above facts explain the favourable results obtained by cautiously adding sulphuric acid to a water containing much bicarbonate. Swelling takes place during dyeing. The solutions given above were used in preparing the dyes. To each dye the same quantity of pure lactic acid was added. The pieces treated with magnesium and sodium chlorides showed scarcely traces of swelling; that from carbonic acid-water remained unchanged; that out of distilled water was satisfactory; those out of calcium carbonate, sulphate, and magnesium carbonate were good; and that from magnesium was extremely good.

The piece treated with magnesium sulphate yielded the best leather; next to this came the piece treated with carbonic acid solution. The pieces from distilled water and the bicarbonates were very much alike, the calcium salt yielding the worst. The pieces from sodium and magnesium chlorides were thinner than the others, and relatively weaker. J. T.

Cleaning of Old Oil-paintings. By E. v. BIBRA (*J. pr. Chem.* [2], xvii, 42—44).—The author, in endeavouring to clean some old pictures in his possession, found that the "putz-wasser" sold for the purpose attacked the pictures, and rendered it necessary to touch them up again with the paint-brush. He employed a method by which a completely indistinct picture was restored, and this he gives as follows:—The picture was freed from dust by a feather, and washed with a sponge and spring water. A layer of soap was then put on (the author recommends shaving soap for this purpose), and allowed to remain eight minutes, after which the soap was washed off with a brush, and the picture left to dry. A small piece of linen cloth was then saturated with nitrobenzene, and with this the picture was cleaned. All dirt was removed, and the picture became distinct, though the colours were dull. Olive oil was then spread over, and a quickly-drying varnish laid on. This method the author applied with equal success to many other pictures. S.

Restoration of Writing in Old Manuscripts. By E. v. BIBRA (*J. pr. Chem.* [2], xvii, 38—40).—The author, after mentioning the importance of this subject, and referring to its value, not merely as a scientific question, but also as a matter of importance in ordinary life, goes on to describe his method. He applies freshly-prepared ammonium sulphide to the indistinct passages, and in a few moments the writing begins to come out clearly. The excess of sulphide is got rid of by the water-bottle, and the moist paper or parchment is then dried at a gentle heat, or between blotting-paper. The writing fades again when thus treated, so the author suggests a solution of tannin applied in the same way. He finds that the writing will last for several months, but for a longer time he cannot vouch, as his experiments were undertaken only a short time since. The above methods, as the author says, are useful only where gall-ink has been employed, but he thinks that this ink was more generally in use, except in the earliest times, than charcoal and indian ink. S.

General and Physical Chemistry.

Thermal Conductivity and Diathermancy of Air and Hydrogen. By HENRY BUFF (*Phil. Mag.* [5], iv, 401—424).—In this paper the author criticises the observations of Magnus, Tyndall, and others upon the above subject. The apparatus used by Magnus, which formed the basis of that on which Buff constructed his own apparatus, is fully described in the beginning of the paper. It consists of a vertical cylinder of glass 56 mm. in diameter, and 160 mm. in height, fused to another glass cylinder of the same width but of a height of 100 mm.; these two cylinders are separated by a thin glass plate. The lower opening of the tube is closed with a cork through which tubes pass, by means of which the gases to be examined may be admitted. An arrangement is also made for the introduction of a thermometer in a horizontal position. The upper part is filled with water which is boiled by a current of steam. To maintain a constant temperature, the apparatus is placed in a beaker and this again in a second vessel containing water at a fixed temperature. Magnus, in experimenting with such an arrangement, found that the heat-rays are partially absorbed by their passage through air: conductive motion, if such existed, was masked by the stronger effect of radiation.

Similar results were obtained by Magnus for the other gases examined by him, except in the case of hydrogen, in which he found that the temperature increases with the increase of density, and that even at the ordinary atmospheric pressure, hydrogen has a greater diathermancy than a vacuum. From this he concluded that hydrogen is similar to the metals as regards its conducting power.

The apparatus used by Buff was similar to that of Magnus, except that he employs a brass cylinder cemented on to the glass vessel, and instead of the thin glass division between the two, he employs a thin metallic plate. The apparatus is packed in cotton-wool to preserve an even temperature. In place of the thermometer used by Magnus, Buff substitutes a thermo-electric pile consisting of German silver and iron wires joined with solder.

The author discusses the observations of Magnus and Tyndall, and gives in a series of tables his numerical results obtained for the different gases examined. With regard to the diathermancy of moist air, his results agree chiefly with those of Magnus, but not with Tyndall's. He finds that the thermal conductivity of hydrogen and of other gases is far too small to admit of its being proved by the method which Magnus adopted. The assumption that the conductivity of hydrogen is similar to that of the metals, if by this statement anything more is meant than that hydrogen, like solid and liquid bodies, is capable of transmitting heat from molecule to molecule, is therefore not justified.

On the other hand hydrogen possesses a diathermancy closely approaching that of a vacuum.

Dry air absorbs from 50 to 60 per cent. of the rays of heat which it receives from a source heated to the boiling-point of water.

The absorptive power of moist air surpasses that of dry air by a trifling percentage, but by no means to such a degree as hitherto assumed by certain physicists.

Rock salt is not absolutely diathermanous for the so-called dark rays of heat, its thermal colour rather resembling that of dark air.

J. M. T.

The Temperature of Flames. By F. Rosetti (*Deut. Chem. Ges. Ber.*, x, 2054).—For the determination of the temperature of flames, an element, consisting of two wires of iron and platinum, each ·3 mm. thick, was inserted in a small porcelain tube closed at one end, and the point of junction of the metals covered with kaolin. The free ends were then connected by means of copper wire with a galvanometer. The instrument was graduated by comparison with a thermometer for the lower temperatures, and for the higher by comparison with the numbers obtained with a calorimeter.

The following results have been arrived at:—

(*a.*) Non-luminous Bunsen flame, 17 cm. long:—

Colourless flame mantle	1350° C.
Violet zone	1250
Inner blue flame	1200

In the dark central cone which had a length of 7 cm.:—

1 cm. above the mouth of the burner	250° C.
2—5 cm. ,, ,, ,,	above 400
6 cm.	650

b. With a closed Bunsen, burning with various mixtures of air and gas, or gas and carbonic acid, the following temperatures were obtained for the hottest part of the flame:—

1 vol. gas and	2	vols. air	1260° C.	
,,	$2\frac{1}{2}$	,,	1150	
,,	3	,,	1116	
,,	4	,,	did not burn.	
,,	$1\frac{1}{2}$	,, Co_2	1000	Flame 7 cm. long.
,,	2	,,	860	
,,	3	,,	780	
,,	4	,,	did not burn.	

T. C.

Incomplete Combustion. By L. Meyer (*Deut. Chem. Ges. Ber.*, x, 2117—2120).—In order to test the accuracy of Bunsen's law, a mixture of water-gas and carbon monoxide was exploded in a eudiometer, and the composition of the residual gases determined. Only 7 experiments were made, and as only 5 of these were performed under similar conditions, no definite conclusions could be deduced. The proportion of the water to that of the carbon dioxide formed is rather higher than in Bunsen's, but lower than in Horstmann's experiments.

W. C. W.

On some Melting-points. By BERTHELOT (*Bull. Soc. Chim.* [2], xxix, 3—4).

1. *Crystallised Phosphoric Acid*, H_3PO_4, melts at 41·75°, and on cooling remains liquid until the temperature reaches 38°, when it solidifies, the temperature rising simultaneously to 40·5°.

2. *Nitric Acid*, HNO_3 (solidified by a mixture of solid carbon dioxide and ether) melts at $-47°$. This temperature is probably too low, owing to the presence of a trace of water.

3. *Chloroform* melts at $-70°$.

4. *Anhydrous Chlorine* melts at $-75°$.

These melting points, with the exception of the first, were determined with an air-thermometer. L. T. O'S.

Vapour-tensions of Compounds. By A. NAUMANN (*Deut. Chem. Ges. Ber.*, xi, 33—35).—The author has shown in former papers that when a substance not miscible with water is distilled in a current of steam, the numbers of molecules of the two substances in the distillate are proportional to their vapour-tensions at the temperature of distillation. According to this law, if w and W represent the actual weights of water and the other body distilled, m and M their molecular weights, and p and P their vapour-tensions,

$$\frac{w}{m} : \frac{W}{M} = p : P; \quad \text{whence } P = \frac{m\,W\,p}{M\,w}.$$

On distilling anthraquinone with steam, it was found in three experiments that the distillate contained, for each 100 grams of water, 0·23, 0·18, and 0·20 gram of anthraquinone, giving for the vapour-tension of the latter body, at 99·7°, 0·15, 0·12, and 0·13 mm.

The vapour-tension of a substance not miscible with water may be arrived at by volatilising it with steam, and deducting from the total observed tension, b, that of water at the temperature of observation, in accordance with the equation

$$P = b - p.$$

The following are examples of vapour-tensions determined by both these methods:—

	Temp.	$\frac{mWp}{Mw}$	$b.p.$
Toluene	84°	331 mm.	336 mm.
Nitrobenzène......	99	19·4 ,,	19·8 ,,
Ethyl benzoate	99·1	15·9 ,,	15·2 ,,
Naphthalene	38·8	18·7 ,,	22 ,,

J. R.

On Vapour-density Determination. By V. MEYER (*Deut. Chem. Ges. Ber.*, x, 2068—2073).—In this process, which is a modification of the method devised by the author for determining the vapour-density of high-boiling bodies (*Deut. Chem. Ges. Ber.*, ix, 1216), the volume occupied by the vapour of a known weight of substance is measured by the quantity of mercury it displaces. For the details of the process the original paper must be consulted. W. C. W.

A New Method of Determining Molecular Weights. By A. NAUMANN (*Deut. Chem. Ges. Ber.*, x, 2099—2102).—The author has recently shown (*Deut. Chem. Ges. Ber.*, x, 1421, 1819, 2014) that when substances which are not miscible with water are distilled in a current of steam, the constituents of the distillate are present in a constant proportion. Theoretical considerations led to the conclusion (since confirmed by experiment) that $\dfrac{\frac{g}{m}}{\frac{G}{M}} = \dfrac{p}{P}$, where g = the weight of one constituent of the distillate, and m = its molecular weight, p = the tension of its vapour at the temperature t of the boiling mixture under the barometric pressure b, G = the weight of the other constituent, M its molecular weight, and P the tension of its vapour at the temperature t. From equation (1) it follows that $M = \dfrac{m\,G\,p}{g\,P}$.

If one of the bodies is water, then $m = 18$, and the value of p will be found in Regnault's tables of the tension of aqueous vapour; g and G are the weights of water and of the substance whose molecular weight is being determined in the distillate; and $P = b - p$. The molecular weight of naphthalene was found by this method to be 113 instead of 128.

The author suggests that in some cases superheated steam might be advantageously employed. W. C. W.

Some Determinations of Molecular Weight. By W. KNECHT (*Deut. Chem. Ges. Ber.*, x, 2073—2074).—The density of the vapours of several high-boiling compounds was determined by v. Meyer's process (*Deut. Chem. Ges. Ber.*, ix, 1216), and the following results were obtained:—

	Retene, $C_{15}H_{13}$.	Fluorene.	Stilbene.	Chrysene.
Calculated	8·10	5·78	6·23	6·42
Found	8·28	5·77	7·89	7·95

W. C. W.

Gay-Lussac's Law of Volumes. By H. SAINTE CLAIRE DEVILLE (*Compt. rend.*, lxxxiv, 1108—1112).—In the discussion which has recently taken place between M. Wurtz and the author respecting the molecular volume of chloral hydrate, it will be remembered that the latter chemist, rejecting the hypothesis of Avogadro, declined to admit that every molecule should correspond with a normal two-volume condensation.

In the present communication, after briefly reviewing the laws of Gay-Lussac, he proceeds to show that, under certain conditions, the *atom* of several elementary bodies is unquestionably capable of occupying different volumes: hence he concludes that it is not unreasonable to suppose that the *molecule* of elementary and of compound bodies may under certain conditions occupy different volumes, and consequently correspond sometimes with a four-volume, sometimes with a two-volume condensation.

It will be admitted by every one, without entering into detailed proof, that the atom of phosphorus and arsenic, as determined by chemical considerations, occupies in the gaseous state half the volume occupied by the atom of chlorine or nitrogen, at the same temperature or pressure; and further, that the volume of the atom of oxygen in the form of ozone, and of sulphur in vapour at low temperatures, is less than the volume of ordinary oxygen and of sulphur-vapour at high temperatures. Why then, says Deville, should we attempt to force ourselves to believe that the molecule of every substance occupies the same volume under similar conditions, seeing that the atoms do not all occupy the same volume, and that it is quite within the bounds of possibility that neither oxygen, sulphur, phosphorus, nor arsenic, as we are acquainted with them, actually exist in such substances as sulphurous anhydride, phosphuretted hydrogen, or arseniuretted hydrogen. He argues further, that the doubling of the atomic weights of oxygen and sulphur, *which was effected solely with the object of maintaining an hypothesis whose inutility can be demonstrated*, is, to say the least, unnecessary; that if the old equivalents be allowed still to represent the atoms, the atomic volumes of sulphur and oxygen are under ordinary conditions one-half of the atomic volumes of some other elements, such as chlorine and nitrogen.

He considers that the vapour-density, as well as the nature of a body, varies with its internal thermic condition; that this variation, taking place in simple multiples only, does not affect the law of Gay-Lussac, while it unfortunately seriously compromises the hypothesis of Avogadro. J. W.

Chemical Equilibrium between Hydrogen and Gaseous Iodine. By G. LEMOINE (*Ann. Chem. Phys.* [5], xii, 145—253).—In this paper the author gives the detailed results of his investigations upon the conditions of chemical equilibrium of hydriodic acid, of which summaries have already been published. Hydriodic acid was chosen as a substance suitable for the study of the general phenomena of chemical equilibrium, since the two constituent elements are monatomic; they combine, or dissociate, without change of volume (at the temperature of the experiment), and the thermal effects of combination are very slight. The aim of the investigation is to show that, under given conditions of temperature and pressure, a mixture of the two constituent gases in given proportions will attain sooner or later a definite state of chemical equilibrium, in which only a certain proportion of the hydriodic acid possible is actually formed, varying with the temperature, pressure, and proportions of the gases present, but always the same for the same conditions. The effects studied are those of heat, pressure, the action of mass, the action of porous bodies, of oxygen, and of light.

Action of Heat and Pressure upon Hydriodic Acid or upon Mixtures of the two Constituents in Equivalent Proportions.—The three temperatures chosen were 440°, 350°, and 260°. When mixtures of equivalent proportions of hydrogen and iodine were heated in closed glass bulbs for several hours, or at low pressures for two or three days at 440°, a state of equilibrium was attained in which between 20 and 30 p.c. of the hydrogen remained free. The effect of pressure was twofold.

At low pressures, the time taken to attain a state of equilibrium was much greater, while the amount of combined gas was somewhat less than at higher pressures. Thus at 4·5 atmospheres, 24 p.c. of hydrogen remained free, while at 0·2 atmosphere 29 p.c. of hydrogen was free. When instead of a mixture of its constituents, hydriodic acid itself was heated, the experiments were not so satisfactory, and the resulting free hydrogen was not quite the same as in the former experiments. At 360° the process was very much slower, the mixture always requiring many days to arrive at a state of equilibrium. The results were similar to those at the higher temperature, but starting from the separated gases, the proportion combined was somewhat greater. When hydriodic acid was heated at 2 atm. pressure, exactly the same quantity of free hydrogen was obtained as was left when the mixture of hydrogen and iodine was heated at the same temperature and pressure, viz., 18·6 p.c. of the total hydrogen present. In the other cases the coincidence was not so close, but still somewhat near. At 260° the combining and dissociating action took place, but so extremely slowly (the time being reckoned by months), that it was almost impossible to prevent accidents to the bulbs, and though the general nature of the phenomena is the same as at higher temperatures, no good determination of the state of equilibrium could be made.

The Action of Mass.—When one of the elements was in excess of its equivalent proportion, it was still found that a definite state of equilibrium was arrived at, and more rapidly than in previous cases, and that the whole of the possible hydriodic acid was never formed, however great the excess of one of the elements. As the proportion of iodine present to the hydrogen present gradually increased, the quantity of hydriodic acid formed gradually increased without any sudden changes in value. The effects of pressure were very slight, but still in the same direction as before.

Action of Porous Bodies.—These seem to act only by bringing the molecules closer together, and, therefore, as is the case with high pressures, they lessen the time of attaining a state of equilibrium, but do not sensibly alter the proportions in that state.

Action of Oxygen.—Oxygen decomposes hydriodic acid, either gaseous or in solution, at ordinary temperatures, though the action is very slow.

Action of Sunlight.—A solution of hydriodic acid is not affected by sunlight, nor does a mixture of iodine and hydrogen combine sensibly. On the other hand, gaseous hydriodic acid is decomposed by sunlight, and since there is no inverse tendency to recombine by the action of light, the decomposition is probably unlimited. In one case by exposure of a bulb to full daylight for a summer month, 80 p.c. of the acid was decomposed. J. H. P.

Is the Decolorising Power of Animal Charcoal due to the Carbon or to Porosity? By F. JICINSKY (*Chem. Centr.*, 1877, 138).—No direct answer is given to the question. The author states that during filtration (of sugar) the organic matters of the syrup, especially the colouring matters, and also the mineral salts, are absorbed by the surface attraction. The lime is withdrawn from the syrup chiefly as calcium hydrate, and partly also as carbonate. In the process of purification the reverse takes place to a certain extent as regards the salts. These are taken away again from the carbon by the water.

In the renovation of the charcoal, the calcium hydrate and carbonate are removed by the acid, and the sugar, together with absorbed organic matters, yields on fermentation first lactic and then butyric acid, thus reducing the complex organic matters to simple compounds. By the action of these acids, a part of the lime is converted into the calcium salts of the fatty acids, and these again are converted on heating into calcium carbonate, and the porosity is restored. The fermentation is much more important than the heating.

G. T. A.

Inorganic Chemistry.

On Media free from Oxygen. By J. W. GUNNING (*J. pr. Chem.* [2], xvi, 314—322).—The object of this paper is to show that no satisfactory method has yet been found for proving the total absence of free oxygen in the vessels used for experimenting on the possibility of life in media free from oxygen. Among reagents proposed for the detection of residual oxygen is Traube's solution of grape-sugar in caustic soda mixed with solution of indigo (*Deut. Chem. Ges. Ber.* (1877), x, 511), but this, according to the author, does not give conclusive results: neither does the method recommended by Gratama (*Onderzoek naar het gevoeligste reagens op zuurstof*, Groningen, 1876), depending on the luminosity of phosphorus, since a piece of phosphorus enclosed in the vacuum of a barometer tube may be rendered luminous again after the luminosity has ceased, by warming the tube or depressing it in the mercury. The author recommends, as a much more delicate test, the white precipitate which potassium ferrocyanide gives at first when mixed with a ferrous salt, and which is rendered blue by the action of oxygen. It is shown that the blue colour is not produced by decomposition of water: and also that the absence of free oxygen in a closed vessel is not warranted by the presence of reducing bodies such as sulphuretted hydrogen and sulphur dioxide.

G. T. A.

Presence of Hydrogen Peroxide in the Atmosphere. By SERGIUS KERN (*Chem. News*, xxxvii, 35).—The experiments were made in a village on the Neva, about twelve versts above St. Petersburgh. The following table shows the quantity of hydrogen peroxide found in rain water during four months:—

Milligrams in one litre of Rain Water.

	Direction of Wind.							
	N.	N.E.	E.	S.E.	S.	S.W.	W.	N.W.
June	0·4	0·3	—	0·3	0·8	0·4	0·5	0·1
July........	0·3	0·1	0·2	0·2	1·4	0·5	0·4	—
August	0·3	—	0·1	0·1	0·3	0·3	—	0·1
September ..	0·1	—	—	0·5	0·7	0·2	0·4	—

The polar winds bring rain poorer in H_2O_2 than the equatorial winds.

The quantitative determinations were made by the method of Schöne (*Cent. Blatt. für Agrikult. Chem.*, June, 1875), which consists in adding to 25 c.c. of the rain water, 0·5 c.c. of a solution containing 5 per cent. potassium iodide, and 0·5 c.c. of a weak aqueous solution of starch. The coloration is compared with a standard solution of hydrogen peroxide. A. J. C.

The Dilatation, Viscosity, and Capillarity of Sulphur. By G. PISATI (*Gazzetta chimica italiana*, vii, 337—343).—The author has carefully determined the expansion of sulphur, his results differing somewhat from those of Moitessier (*Recherches sur la dilatation du soufre*). This is to be attributed to the fact that the latter, in order to expel the air, boiled his sulphur in the dilatometer, whilst the author, who employed crystals of native Sicilian sulphur, removed the air by means of the air pump. A table of the results obtained by the author with the sulphur crystals, and with sulphur modified by boiling, is given, and the difference in the increment of volume for equal increments of temperature in the two varieties is very remarkable. At temperatures ranging from 135° to 185° the minimum for virgin sulphur is at about 159·5°, whilst for sulphur altered by boiling it is 165°.

In the case of capillarity, also, the results obtained with virgin sulphur differ greatly from those with modified sulphur. For the virgin sulphur there is a minimum at 157°, and a maximum at 171°, whilst with the modified sulphur the capillarity is generally greater than with the virgin sulphur; with elevation of temperature it increases slowly at first, more rapidly at 158°, and attains a maximum at 175°.

The viscosity of the sulphur was determined in two ways:—1. By observing the time required for a hollow platinum ball to sink 0·25 meters in fused sulphur. 2. The time required for the sulphur to rise in a capillary tube, under a known pressure. It was found that the viscosity of virgin sulphur attained a minimum at 157°, then increased rapidly, attaining a maximum at 195°. The viscosity of modified sulphur is generally more feeble than that of virgin sulphur, attaining a minimum at 155°, and a maximum at 200°. C. E. G.

On a Liquid contained in an Ancient Glass Vase. By BERTHELOT (*Bull. Soc. Chim.* [2], xxix, 6—9).—The vase, which was sealed up, contained a clear, colourless, neutral liquid, having an insipid taste. It contained no organic matter, but on evaporation left a residue, which consisted principally of sodium sulphate, mixed with a small quantity of calcium sulphate, and traces of silica and sodium chloride.

The presence of silica and sodium sulphate is due to the action of the water on the glass, whilst the calcium sulphate and sodium chloride were, probably, previously in the liquid.

L. T. O'S.

Hyponitrous Acid. By J. D. van der Plaats (*Deut. Chem. Ges. Ber.*, x, 1507—1508).—Divers, in 1871 (*Proc. Roy. Soc.*, xix, 425), prepared the silver salt of this acid by the action of sodium amalgam upon solutions of the alkaline nitrates, and subsequent precipitation with silver nitrate, in presence of acetic acid. The author, who has adopted the same method, appears to have obtained this salt in the pure state. Five analyses are given, all agreeing closely with the theoretical requirements of the formula, AgNO (Divers' analyses showed a deficit of 1 per cent. Ag). It is an amorphous solid, of a pale yellow colour, and is not decomposed by exposure to diffused light. It may be boiled with water, without undergoing decomposition: above 110° it appears to be decomposed, with formation of silver nitrate; if heated suddenly to 150° it decomposes with explosion and evolution of brown vapours. It is soluble in dilute nitric and sulphuric acid, and is precipitated unchanged on neutralising the solution. Sodium hydrate is without action on this body at temperatures below 70°. An aqueous solution of the free acid is obtained by decomposing the silver salt, held in suspension in water, by an equivalent of hydrochloric acid. This solution liberates iodine from potassium iodide, and reduces potassium permanganate. It undergoes spontaneous decomposition, gradually at ordinary temperatures, probably according to the equation, $2HNO = H_2O + N_2O$. This resolution is at once determined by the action of concentrated sulphuric acid, both on the aqueous acid and the silver salt. This establishes the formula HNO as expressing the composition of the acid. C. F. C.

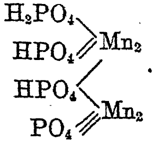
Studies on the Phosphates. By E. Erlenmeyer (*Liebig's Annalen*, cxc, 189—190).—Phosphoric acid, being triatomic and bibasic, is capable of forming three series of salts, viz.:—

Mono-	Di-	Tri-metallic phosphates.
$(PO_4H_2)Me$	$(PO_4H)Me_2$	$(PO_4)Me_3$.

If the metal or radicle of the base is univalent, the three salts are formed by the action of 1 mol. phosphoric acid on 1, 2, or 3 mols. of base respectively. If the radicle of the base is bivalent, the formation of the mono- and tri-metallic phosphates requires 2 mols. phosphoric acid to 1 or 3 mols. of base, but the dimetallic phosphate may be formed by the action of 1 mol. phosphoric acid on 1 mol. of base. In the case of trivalent metals, the formation of the mono- and di-metallic phosphates requires 3 mols. phosphoric acid to 1 and 2 mols. base respectively, but the trimetallic phosphate may be formed with 1 mol. base to 1 mol. phosphoric acid. If the radicle of the base is quadrivalent, the di- and tri-metallic phosphates are formed from 4 mols. phosphoric acid and 1 or 3 mols. of base—the dimetallic salt from 2 mols.

acid to 1 mol. base—and for sexvalent metals or radicles, the formation of the mono-, di-, or tri-metallic salt requires 6, 3, and 2 mols. phosphoric acid to 1 mol. of base.

Hence it appears that to form the smallest possible molecules of simple phosphates of polyacid bases, several molecules of phosphoric acid are for the most part required to 1 mol. of base; and since the phosphates of one series which contain 1 molecule of phosphoric acid, may, by the influence of bases, or even of water, be changed into those of another series, so it appears probable that in phosphates formed of several molecules of phosphoric acid united with a polyacid base, the change from one series to another may be only partial, and that a "combined" salt may result, belonging at once to two or more different series. Thus, in the case of manganese phosphates, it is possible to suppose the existence of a phosphate whose molecule is built up of mono-, di-, and tri-manganese phosphate,



$$\begin{matrix} H_2PO_4 \\ HPO_4 \\ HPO_4 \\ PO_4 \end{matrix} \begin{matrix} > Mn_2 \\ \\ > Mn_2 \end{matrix}.$$

The following investigation has demonstrated the existence of such "combined" salts, which on the one hand are mono-di-, and on the other, di-tri-metallophosphates.

Manganese Phosphates. By E. ERLENMEYER and O. HEINRICH (*Liebig's Annalen*, cxc, 191—211).—Monomanganese phosphate is prepared by heating moist manganese sulphide with phosphoric acid; it separates from the red solution as a crust, consisting of concentric groups of four-sided prisms; excess of phosphoric acid was removed by washing with ether. This compound has the composition, $Mn_2(PO_4H_2)_4 + 4H_2O$, thus agreeing with the results of Heintz (*Pogg. Ann.*, lxxiv, 450). When heated to 100° it loses not only water, but phosphoric acid. When exposed to the air it undergoes no change, but if the air be saturated with moisture, it dissolves to form an acid solution, from which rose-coloured crystals separate out, possessing a glassy lustre, and having the composition, $Mn_2(PO_4H)_2 + 6H_2O$. This dimanganese phosphate is also formed when the monophosphate is treated with water; this latter compound Heintz described as soluble in water. This error must have arisen from his monophosphate containing free acid, since even on treatment with large quantities of water, the dimanganese phosphate separates out. The filtrate from the crystals of the diphosphate formed by action of water on the monophosphate, yields, when boiled for some time, rose-coloured monoclinic prisms of the di-trimanganese phosphate $(Mn_2)_5(PO_4)_4(PO_4H)_4 + 8H_2O$.

Dimanganese Phosphate.—Monomanganese phosphate, when boiled with alcohol, as already shown by Heintz, forms the diphosphate. This compound may also be prepared in the crystalline state, by precipitating a manganese salt with disodic phosphate, and dividing the fluid and precipitate into two portions, one portion being treated with hydrochloric acid till the precipitate is dissolved, and the other portion added to this, whereupon, after a while, flesh-coloured plates separate out; or according to Debray's method, which consists in adding alcohol to a solution of monomanganese phosphate containing free phosphoric acid, crystals of the diphosphate then separating out. After some time the crystals of the diphosphate have the composition $Mn_2(PO_4H)_2 + 6H_2O$; and, according to Haushcfer, belong to the rhombic system. By the action of water in the cold, trimanganese phosphate is formed, whilst by the action of boiling water, di-trimanganese phosphate, $(Mn_2)_5(PO_4)_4(PO_4H)_4 + H_2O$, is obtained.

Trimanganese Phosphate.—This salt was obtained by Heintz's method, viz., by the precipitation of manganese sulphate with an excess of disodic phosphate. Its composition is $(Mn_2)_3(PO_4)_4 + 14H_2O$; when dried over sulphuric acid it loses 7 molecules of water. The triphosphate obtained by the action of cold water on the diphosphate differs from the salt prepared by Heintz's method in losing, on exposure to the air, quantities of water varying with the state of the air, but resembles it in losing 7 molecules of water when dried over sulphuric acid.

The authors do not find that boiling water acts on mono- or di-manganese phosphate to form trimanganese phosphate, as stated by Debray; in each case di-trimanganese phosphate, $(Mn_2)_5(PO_4)_4(PO_4H)_4 + 8H_2O$, is formed.
P. P. B.

The Sulphates of Vanadium Tetroxide. By B. W. GERLAND (*Deut. Chem. Ges. Ber.*, x, 2109—2116).—When a solution of vanadium tetroxide in excess of sulphuric acid is heated for several hours to the boiling point of sulphuric acid, vanadyl sulphate, $V_2O_2.2SO_4$, separates out in the form of a dirty greenish-blue, sandy powder, insoluble in water and in hydrochloric and sulphuric acids.

A clear, greenish-blue modification of this sulphate is obtained by heating the greenish-blue powder at 400° for 12 hours. In this state it dissolves completely when heated with water in sealed tubes to 130°, forming a deep blue solution, which, on evaporation over sulphuric acid, leaves a hard, resinous, transparent mass.

Vanadyl sulphate unites with 3, 4, 7, 10, and 13 molecules of water. $V_2O_2.2SO_4.7H_2O$, described by Crow (this *Journal*, 1876, ii, 456), is formed when the resinous mass just mentioned is moistened with water, or dilute alcohol. On exposure to moist air, crystals containing 13 molecules of water of crystallisation are obtained.

$V_2O_2.2SO_410H_2O$ was deposited in large, deep blue crystals by the spontaneous evaporation of a solution of the amorphous sulphate. When heated at 100°, the crystals rapidly lose 5 molecules of water, and 2 more are slowly expelled at the same temperature, but the remaining 3 molecules are not driven off at 130°.

Three acid vanadyl sulphates are known, viz., $V_2O_2H_23SO_45H_2O$ (described by Crow, *loc. cit.*), $V_2O_2H_23SO_43H_2O$, and $V_2O_2H_23SO_42H_2O$. A solution of vanadium tetroxide in excess of sulphuric acid, after being heated at 120° for several hours, forms a crust of deliquescent, blue, transparent crystals, having the composition, $V_2O_2H_23SO_43H_2O$. A solution of this sulphate is decomposed by dialysis, losing sulphuric acid.

The blue crust is partly dissolved by water, but leaves a residue, consisting of shining scales of the sulphate containing 2 molecules of water of crystallisation. The same compound is easily obtained by heating the sulphuric acid solution of vanadium tetroxide at 140—160°, for several hours.

The acid vanadyl sulphates, on precipitation, carry down other salts contained in solution. Double salts of vanadyl sulphates with sodium, potassium, and magnesian sulphates could not be prepared.

W. C. W.

Note on Metallic Niobium and a New Niobium Chloride. By H. E. Roscoe (*Chem. News*, xxxvii, 25).—It is to Marignac and Bloomstand that we owe a deliverance from the state of contradiction and uncertainty that surrounded the metals existing in such minerals as columbite and tantalite. They have independently proved that only two metals in reality exist—niobium and tantalum, and that all the other supposed metals, pelopium, decinium, and ilmenium, are either simple mixtures of niobium and tantalum in varying proportions, or such a mixture containing, in addition, some other metals, such as tungsten, titanium, or iron.

Niobium pentoxide (Nb_2O_5), niobium pentachloride ($NbCl_5$), and niobium oxychloride ($NbOCl_3$), as well as metallic niobium, and a new chloride of niobium, were prepared from several crystals of Greenland columbite, which has a specific gravity of 5·389, and contains, as Marignac has shown, little or no tantalum.

The following results of analysis of the pentachloride and oxychloride serve to show the purity of the material:—

	Pentachloride.	
	Calculated.	Found.
Nb ..	34·62	34·38
Cl ..	65·38	65·55
	100·00	99·93

	Oxychloride.	
	Calculated.	Found.
Nb	43·42	42·93
Cl	49·19	49·34
O (diff.) .	7·39	7·73
	100·00	100·00

Metallic niobium is obtained as a bright steel-grey, shining, metallic crust, by passing the vapour of the pentachloride mixed with hydrogen, repeatedly through a red-hot glass tube. The metallic crust is then strongly ignited in a porcelain tube in a current of hydrogen until no further evolution of hydrochloric acid occurs. Special precautions are necessary to avoid as completely as possible access of traces of oxygen.

The metal, which had been prepared by two distinct operations, was analysed by converting it into the pentoxide by ignition in a current of air; the results of two analyses gave 96·14 and 97·18 per cent. of niobium respectively. Niobium takes fire and burns brightly to the pentoxide, a small trace of oxychloride being usually deposited from an impurity in the metal. When the metal was allowed, in one instance, to oxidise very slowly, the formation of an indigo-blue lower oxide was first observed, but on further heating this passed into the yellow pentoxide.

The metal thus prepared contained only 0·27 per cent. of hydrogen, thus proving it was not a hydride, as has been supposed. Metallic niobium is of a steel-grey colour, with a bright metallic lustre. It is not attacked in the cold by either dilute or concentrated hydrochloric or nitric acid, or by aqua regia. Strong sulphuric acid quickly dissolves the metal, forming a colourless solution. At the ordinary temperature niobium does not take fire in chlorine gas, but it does so when gently heated, with formation of pentachloride and a trace of oxychloride, owing to the unavoidable presence of a small quantity of oxygen in the metal. The specific gravity of metallic niobium is 7·06 at 15·5°.

Niobium trichloride, $NbCl_3$. The vapour of niobium pentachloride when passed through a heated glass tube, is slowly decomposed, with formation of a black deposit of trichloride. Niobium trichloride is generally obtained as a black crystalline crust, having almost a metallic lustre, and closely resembling a film of sublimed iodine; it is sometimes deposited in long needle-shaped crystals, which exhibit a dichroic lustre. The trichloride is non-volatile; it is not deliquescent, and is not decomposed by water or ammonia. Dilute nitric acid at once converts it into niobic and hydrochloric acids. When heated in the air it emits dense fumes.

The analysis of the trichloride was made by decomposing it, in some cases, by nitric acid directly, and in other cases by fusion with sodium carbonate, and treating the fused mass with nitric acid. The numbers obtained in three experiments closely approximate to those required by the formula $NbCl_3$.

When the vapour of niobium oxychloride is passed over red-hot charcoal in an atmosphere of carbon dioxide, no change occurs, but the pentachloride is obtained when the carbon dioxide is replaced by chlorine.

A remarkable action occurs when the trichloride is heated in a current of carbon dioxide; this gas is decomposed, and a white sublimate of oxychloride is obtained with the corresponding quantity of carbon monoxide. The oxychloride on analysis gave Nb = 3·48 p.c.; Cl = 47·03; O = 9·49.

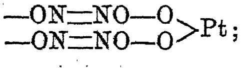
In two experiments the quantity of the gas obtained was found to correspond closely with the theoretical amount.

A decomposition of carbon dioxide by a metallic chloride has hitherto not been observed. Phosphorus trichloride absorbs free oxygen on distillation in the air, with formation of oxychloride, but does not decompose carbon dioxide. A. J. C.

Density of Solid Mercury. By J. W. MALLET (*Phil. Mag.* [5], iv, 145—151).—The specific gravity of solid mercury as given by different authorities varies between 14 and 15·19. Schulze obtained experimentally the number 14·391, but does not mention the temperature; Biddle's result was 14·485 at —60° C., a temperature whose correctness is doubtful, if not improbable. The imperfections of the instruments employed, and the comparative ignorance of the constants necessary for correction at the time these determinations were made, render the exactness of the above results very questionable. In redetermining the specific gravity of solid mercury, the author employed a cylindrical glass flask of about 58 c.c. capacity, connected by a narrow glass tube with a smaller reservoir of about 25 c.c. capacity; the latter vessel was accurately stoppered. The capacity of the larger vessel, when filled up to a fine mark on the connecting tube, was determined by weighing water and mercury in it: the cubical coefficient of expansion of the glass was found by weighing it, filled to the mark with mercury at different temperatures. Using a carefully corrected alcohol thermometer, the density of alcohol at −39° was taken, and then its coefficient of expansion for temperatures near that required for freezing mercury was found. A quantity of mercury, weighing 558·9353 grams, and carefully purified by nitric acid and subsequent distillation, was now introduced into the apparatus; alcohol was poured upon the mercury, and brought exactly to the mark when the mercury was frozen and all alteration in the height of the alcohol had ceased, the temperature of the freezing-mixture being at the same time accurately noted. After regaining the temperature of the room the apparatus was weighed: the weight of alcohol contained in it was found by substracting the weight of the glass and the weight of the mercury; the volume of alcohol, calculated from data mentioned above, when substracted from the corrected volume of the larger vessel, gave the volume of the known weight of solid mercury.

The mean of three closely concordant results is 14·1932, this number representing the density of solid mercury at its fusing point as referred to water at 4° C. taken as unity. F. C.

Platonitrites and Diplatonitrites. By L. F. NILSON (*J. pr. Chem.* [2], xvi, 241—278).—In the year 1861 Lang discovered a double salt of platinum, which was produced on heating mixed solutions of potassium platinochloride and potassium nitrite (*J. pr. Chem.*, lxxxiii, 415). The composition of the salt was found to agree with the formula $K_2Pt(NO_2)_4$, but its constitution was not then understood. Blomstrand afterwards (*J. pr. Chem.* [2], iii, 186) assigned to the salt, on theoretical grounds, the formula $(K—O—NO=NO—O)_2Pt$, in which the platinum plays the part of a diatomic element; and this formula was supported by the fact, discovered by Blomstrand, that the salt readily takes up two atoms of chlorine or bromine to form a compound of tetratomic platinum. On this view the salt may be regarded as containing the negative radicle *platotetranitrosyl*—



$$\begin{matrix}—ON=NO—O \\ —ON=NO—O\end{matrix}\!\!>Pt;$$

and accordingly the corresponding acid may be called *platotetranitrous*, or simply *platonitrous acid*, and its salts *platonitrites*.

The following platonitrites have been prepared and analysed by the author. Except where otherwise stated, they were obtained by decomposing barium platonitrite with the sulphates of the respective bases.

Potassium Salt, $K_2.4NO_2.Pt$.—Crystallises from mixed solutions of potassium platinochloride and potassium nitrite in small colourless brilliant four- or six-sided prisms. It crystallises without water from a solution of potassium chloride, but with 2 mols. of water from aqueous solution.

Rubidium and Cæsium Salts, $Rb_2.4NO_2.Pt$ and $Cs_2.4NO_2.Pt$.—Obtained by decomposing silver platinonitrite with rubidium or cæsium chloride. Crystallise in small colourless or faintly-yellow transparent needles, which are permanent in the air and at 100°, and dissolve sparingly in water. The rubidium salt crystallises with 2 mols. of water on spontaneous evaporation of a dilute solution.

Ammonium Salt, $(NH_4)_2.4NO_2.Pt + 2H_2O$.—Formed by triturating equivalent proportions of silver platonitrite and ammonium chloride with a little water. Crystallises in brilliant colourless or yellowish six-sided rhombic prisms, which are permanent in the air, but lose their water over sulphuric acid. The salt is decomposed with explosive violence when heated in the slightest degree over an open flame, leaving a bulky residue of spongy platinum.

Thallium Salt, $Tl_2.4NO_2.Pt$.—Crystallises in small brilliant, colourless, semi-transparent prisms, very sparingly soluble in cold water, and stable in the air and at 100°.

Sodium Salt, $Na_2.4NO_2.Pt$.—From the silver salt and sodium chloride. Crystallises in long colourless six-sided rhombic prisms, easily soluble in water, and permanent at 100°.

Lithium Salt, $Li_2.4NO_2.Pt + 3H_2O$.—Obtained as the last. Crystallises in beautiful short rhombic prisms, which dissolve easily in water, turn moist in the air, and give off their water of crystallisation at 100°.

Silver Salt, $Ag_2.4NO_2.Pt$.—Obtained by decomposing potassium platonitrite with silver nitrate, and crystallising the product repeatedly in presence of excess of silver nitrate. Small yellowish monoclinic four-sided prisms, permanent in the air, and sparingly soluble in cold water.

Calcium Salt, $Ca.4NO_2.Pt + 5H_2O$.—Obtained by double decomposition of the silver salt and calcium chloride. Forms thin yellowish oblique four-sided prisms, which are permanent in moist air, but effloresce over sulphuric acid, and lose the whole of their water at 100°. The salt is very easily soluble.

Strontium Salt, $Sr.4NO_2.Pt + 3H_2O$.—Obtained as the last. Forms large colourless or yellowish six-sided prisms, which dissolve easily in water, lose two-thirds of their water at 100°, and bear a high temperature without decomposition.

Barium Salt, $Ba.4NO_2.Pt + 3H_2O$.—Obtained as the calcium salt. Crystallises very readily in colourless brilliant tables or prisms, sparingly soluble in cold water, and permanent in the air.

Lead Salt, $Pb.4NO_2.Pt + 3H_2O$.—Obtained as the calcium salt. Crystallises over sulphuric acid in yellow opaque six-sided monoclinic prisms, which lose their water at 100°.

Magnesium Salt, $Mg.4NO_2.Pt + 5H_2O$.—Colourless transparent six-sided monoclinic prisms, easily soluble in water, permanent in the air and at 100°, but decomposed by gentle heating, swelling up enormously.

Manganese Salt, $Mn.4NO_2.Pt + 8H_2O$.—Crystallises in beautiful large rose-red triclinic prisms, which gradually turn darker in the air. Blackens at 100°, evolving nitric oxide.

Cobalt Salt, $Co.4NO_2.Pt + 8H_2O$.—Forms large red prisms, isomorphous with the last. Easily soluble in water; permanent in the air; decomposed at 100°.

Nickel Salt, $Ni.4NO_2.Pt + 8H_2O$.—Beautiful green transparent very thin tables or laminæ, which are easily soluble in water and permanent in the air, but decomposed at 100°, giving off red vapours.

Copper Salt (basic) $3(Cu.4NO_2.Pt) + CuO + 18H_2O$.—From the barium salt and cupric sulphate. Crystallises in golden-yellow delicate needles, which are decomposed by water, giving a green solution and a dark-coloured precipitate.

Copper Salt (normal), $Cu.4NO_2.Pt + 3H_2O$.—Crystallises from the mother-liquor of the preceding salt in very small green needles, which dissolve easily in water. Decomposed at 100°.

Zinc Salt, $Zn.4NO_2.Pt + 8H_2O$.—Large colourless or yellowish transparent crystals, isomorphous with those of the manganese, cobalt, and nickel salts. Easily soluble in water. Decomposed at 100°.

Cadmium Salt, $Cd.4NO_2Pt + 3H_2$.—Large yellow transparent monoclinic prisms, easily soluble in water, and efflorescent in the air. Gives off its water at 100° without further decomposition.

Mercurous Salt, $Hg_2.4NO_2.Pt + Hg_2O + H_2O$.—Precipitated on mixing solutions of potassium platonitrite and mercurous nitrate. Small pointed prisms nearly insoluble in water, and becoming anhydrous at 60°.

Aluminium Salt, $Al_2.(4NO_2.Pt)_3 + 14H_2O$.—Large colourless apparently cubical crystals, very easily turning red owing to formation of diplatonitrite (see below). Decomposed at 100°.

Yttrium Salt, $Y_2.(4NO_2.Pt)_3 + 9H_2O$.—Small lemon-yellow oblique four-sided prisms, permanent in the air and easily soluble in water. The mother-liquor deposits a salt with 21 mols. of water, in long colourless or yellowish crystals, which lose 18 mols. of water at 100°.

Erbium Salt, $Er_2.(4NO_2.Pt)_3 + 9H_2O$.—Small yellow oblique four-sided prisms, easily soluble in water and permanent in the air. Another salt containing 21 mols. of water is deposited from the mother-liquor in large reddish crystals.

Cerium Salt, $Ce_2.(4NO_2.Pt)_3 + 18H_2O$.—Yellowish oblique four-sided tables or rhombohedrons, easily soluble in water. The salt quickly undergoes alteration in the air and loses 15 mols. of water at 100°.

Lanthanum Salt, $La_2.(4NO_2.Pt)_3 + 18H_2O$.—Closely resembles the preceding. Dissolves very easily in water, and deliquesces in moist air.

Didymium Salt, $Di_2.(4NO_2.Pt)_3 + 18H_2O$.—Resembles the last two. Easily soluble in water; permanent in dry air; loses five-sixths of its water at 100°.

Beryllium, ferrous, ferric, and indium platonitrites could not be prepared, owing to the tendency of their solutions to give off nitrous acid and form more stable compounds, as represented by the general equation—

$$2(R{-}O{-}NO{=}NO{-}O)_2Pt = (R{-}O{-}NO{=}NO{-}O{-}Pt)_2O + 2(R.O.NO) + N_2O_3.$$

The new salts thus formed are called by the author *diplatonitrites*, the negative radicle in them containing twice as much platinum as the radicle of the platonitrites. Some of the platonitrites described above are also partially decomposed in such a manner as to yield diplatonitrites when their solutions are heated. Of this class of salts the following have been analysed.

Beryllium Salt, $Be.(2NO_2.Pt)_2.O + 9H_2O$.—Red prismatic crystals, sparingly soluble in water, forming a bright-yellow solution. Loses two-thirds of its water at 100°.

Ferric Salt, $Fe_2.(2NO_2.Pt)_6.O_3 + 30H_2O$.—Resembles the beryllium salt. Easily soluble in hot water. Loses four-fifths of its water at 100°.

Indium Salt, $In_2.(OH)_2.(2NO_2.Pt)_4.O_2 + 10H_2O$.—Very small red needles sparingly soluble in water, forming an orange-red solution.

Silver Salt, $Ag_2.(2NO_2.Pt)_2.O$.—Tufts of greenish very small four-sided prisms, insoluble in water.

Aluminium Salt, $Al_2.(OH)_2.(2NO_2.Pt)_4.O_2 + 10H_2O$.—Brilliant orange-red small needles, permanent in the air, easily soluble in hot water and alcohol.

Chromium Salt, $Cr_2.(OH)_2.(2NO_2.Pt)_4.O_2 + 24H_2O$.—Small red crystals forming a greenish-violet solution in water. Gives off 18 mols. of water at 100°.
J. R.

Mineralogical Chemistry.

Bischofite, a New Mineral from the Stassfurth Mines. By E. PFEIFFER (*Arch. Pharm.* [3], xi, 296—305).—Bischofite, or hydrated magnesium chloride, is found with carnallite in cavities, and as a crust on rock-salt in the above mines. The crystals of bischofite often contain microscopic crystals of sodium chloride, and may be distinguished from carnallite by the fact that they are very deliquescent, harden on exposure to a temperature of 40—45°, but deliquesce when the temperature falls: this property is not possessed by carnallite. The colour is white or transparent, hardness 1·7, and specific gravity 1·65; when heated, they give off water and hydrochloric acid, becoming opaque at the same time. The composition of bischofite appears to be $MgCl_2 + 6H_2O$. When heated on platinum it leaves a residue of magnesium oxychloride. A description of the position of the layers in which this mineral and carnallite are found is also given.
E. W. P.

Penetration Twins of Orthoclase, from Cornwall. By H. LASPEYRES (*Jahrb. f. Min.*, 1877, 529—530).—The author examined a fine pseudomorphous penetration-twin crystal of tin-stone after orthoclase, from Redruth, Cornwall, and found the twin law to be one entirely new to orthoclase, viz.: "the twin-plane a face of ∞P." The two halves of this penetration-twin were extremely well developed contact-twins according to the Carlsbad law, viz.: "the two individuals of each Carlsbad-twin being a right and left crystal."
C. A. B.

Crystals of Analcime from the Kerguelen Islands. By H. LASPEYRES (*Jahrb. f. Min.*, 1877, 530).—Fine crystals of analcime from the above-mentioned locality, 10 mm. in size, often exhibit on the cubical edges of 202, very narrow but well defined faces of the form $\frac{3}{2}$O. No other faces are observed. This triakisoctohedron $\frac{3}{2}$O is the first observed to occur on analcime. C. A. B.

An Analysis of a Crystal of Desmine of Unusual Form from the Faroe Islands. By HEDDLE (*Jahrb. f. Min.*, 1877, 530—531). Crystals of desmine are generally tabular through the predominance of $\infty P\breve{\infty}$, but the specimen in question was characterised by the predominance of $\infty P\bar{\infty}$. Spec. gr. = 2·103. Chem. comp. as follows, viz.:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	K_2O.	Na_2O.	H_2O.
58·79	14·613	0·47	9·534	0·232	0·324	17·298 = 101·261

The desmine analysed by Heddle is found on Bordoe, south-west of the Bay of Waii or Hoiwig, in amygdaloid, accompanied by large rhombohedrons of chabasite. C. A. B.

Homilite, a Mineral from Brevig, Norway. By S. R. PAIJKULL (*Jahrb. f. Min.*, 1877, 536—537).—This mineral is accompanied by erdmannite and melinophane, and occurs at Stockoe, near Brevig. Colour, black to brownish-black. Resinous to vitreous lustre, and only slightly transparent in thin fragments. H. = 5·5. Spec. gr. 3·28. Fuses easily to a black glass, and is completely and easily decomposed by hydrochloric acid. Chem. comp. as follows, viz.:—

SiO_2.	FeO.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	Loss on ignition.	B_2O_3.
31·875	16·25	2·145	1·50	27·275	0·52	1·09	0·41	0·41	18·085 = 100·00;

from which result (after deducting Fe_2O_3) the formula—

$$3(CaO.FeO).2SiO_2.B_2O_3,$$

is obtained. Homilite crystallises either in the rhombic or in the monosymmetrical system, according to A. E. Nordenskiöld, the inclination of the vertical axis to the clinodiagonal being almost 90°. $a : b : c = 1 : 0·6362 : 0·6473$. The forms observed were $\infty P\bar{\infty} . \infty P . \infty P\breve{2} . P . P\breve{2} . P\breve{\infty}$. The angles for these forms measured and calculated are as follows, viz.:—

	Observed.	Calculated.
$\infty P : \infty P\breve{2} =$	160° 48′	160° 38′
$\infty P\breve{2} : \infty P\breve{2} =$	103° 41′	103° 40′
$\infty P\breve{2} : P\breve{\infty} =$	115° 18′	115° 18′
$P\breve{\infty} : P =$	116° (about)	162° 38′
$\infty P : P =$	139° 39′	140° 20′

Homolite therefore closely resembles datolite both chemically and crystallographically. C. A. B.

Mineralogical Notes. By A. E. NORDENSKIÖLD (*Jahrb. f. Min.*, 1877, 537—538).—*Thorite, from the Felspar-quarry, near Arendal.* This mineral is accompanied by fergusonite and orthite, and occurs in large reddish-brown zircon-like crystals, attached to black mica, and enclosed in ochre-coloured orthoclase. One crystal measured 63 mm. in length, and exhibited the form ∞P.P, the faces being rough and dull. The substance of these crystals is isotropic, so that they can be classed as pseudomorphs, most probably of thorite after zircon. The occurrence of amorphous substances in quadratic, rhombic, and monosymmetrical forms is peculiar to many minerals (containing rare elements) which are found in pegmatitic veins. Thorite from Arendal is resin-brown, almost opaque, dull, with a resinous lustre, easily soluble in hydrochloric acid. Fracture slightly conchoidal. H. 4·5. Spec. gr. 4·38. Chem. comp. as follows, viz.:—

SiO_2.	P_2O_5.	CaO.	MgO.	Ce_2O_3.	Thoria.	Mn.
17·04	0·86	1·99	0·28	1·39	50·06	trace

Fe_2O_3.	UrO.	PbO.	H_2O.
7·60	9·78	1·67	9·46 = 100·13

From this result it appears that Arendal thorite probably contains apatite, limonite, and a compound of lead.

Crytolite from Ytterby.—Found in company with fergusonite, xenotime and arrhenite in very brittle quadratic crystals which are generally attached to black mica. The crystals are yellowish-brown, transparent, and appear to be a combination of the prism and pyramid of the second order, with a dodecahedral type. H. = 5·5—6. Spec. gr. 3·29. Chem. comp. as follows, viz.:—

SiO_2.	ZrO_2.	Erbia and Yttria.	Ce_2O_3.	CaO.	MgO.	FeO.	H_2O.
27·66	41·78	8·49	3·98	5·06	1·10	trace	12·07 = 100·14

Be_2O_3 is not present.

C. A. B.

Manganosite and Pyrochroite from the Mossgrube, Nordmark, Wermland. By A. SJÖGREN (*Jahrb. f. Min.*, 1877, 538—539).—These rare minerals were found in a porous limestone-rock which is both weathered and massive. They are accompanied by a peculiar greenish-yellow or brownish garnet, and a microscopical olivine-like mineral, the whole occurrence exactly resembling that of Laangbanshytta. C. A. B.

Perowskite as a Microscopical Constituent of Bohemian Nepheline-picrite. By E. BORICKY (*Jahrb. f. Min.*, 1877, 539—540).—The specimens examined came from the neighbourhood of the Devin, near Wartenberg, and closely resembled (mineralogically and chemically) the picrite of Tschermak, differing however from that particular rock in the constant occurrence of nepheline and perowskite. The latter mineral is found in sharply defined crystals, having a diameter of 0·01 to 0·02 mm., with a greyish-white, violet-grey, or yellowish-brown colour in transmitted light; the centre of each crystal appearing black and impellucid. The streak of perowskite is blackish-grey, semi-metallic, with a strong shimmering lustre. It is also one of the first formations from the magma of the nepheline-picrite, being embedded in the nepheline, olivine, and biotite mixture, and having undergone no perceptible change with the alteration of the surrounding magma or cement. Olivine is one of the chief constituents of nepheline-picrite, and the outlines of its crystal sections are mostly fresh, whilst the nepheline crystal-outlines, on the contrary, generally exhibit a more or less complete decomposition and various enclosures. The constitution of the nepheline-picrite is as follows:—Olivine, 37 per cent.; nepheline, 13 per cent.; biotite, 3 per cent.; magnetite, 5 per cent.; iron pyrites, 0·2 per cent.; apatite, 2·8 per cent.; perowskite, 4·5 per cent.; picotite, 1·5 per cent.; cement, 32 per cent. Total, 99·0 per cent.

The author points out that this is the first time that perowskite has been found in an eruptive rock. C. A. B.

The Lherzolite, or Olivine-rock of the Ariège (Pyrenees). By BONNEY (*Jahrb. f. Min.*, 1877, 540—541).—Zirkel described the mineralogical and geological characteristics of this rock (*Jahrb. f. Min.*, 1867, 746); but Bonney made a microscopical examination of it, and found it to contain olivine, enstatite, diopside, picotite, and particles of a mineral resembling magnetite.

Microlites are rare. The olivine occurs in round grains, the diopside with crystalline outlines, and the enstatite with long irregular outlines. The olivine has apparently crystallised out the first, and the picotite the last; the former sometimes contains peculiar worm-like hollows, which are occasionally empty, and also occasionally filled with a brown substance. The enstatite is colourless (in polarised light, light grey or blue), granular, has a distinct cleavage parallel to $\infty P \breve{\infty}$, and contains peculiar zones penetrating the easiest cleavage direction at right angles, and no doubt brought about by long fine hollows, or through microlites. The diopside has a beautiful green colour in thin sections, and a distinct cleavage direction. The picotite occurs in irregular isolated grains of a dark-green or brown colour, and penetrated by distinct cracks. The olivine constitutes about two-thirds of the whole rock, and is often partially decomposed into serpentine. C. A. B.

Mineralogical Notices from Elba. By G. ROSTER (*Jahrb. f. Min.*, 1877, 531—536).—The minerals described below are either entirely new to Elba, or from hitherto unknown localities in that island.

Picroalumogen is a new species which the author discovered in aluminous slate in the iron-mine of Vigneria, not far from some masses of serpentine, and associated with sulphur and melanterite as products of the decomposition of iron-pyrites. It occurs in stalactitic, knotty, radio-fibrous, semi-transparent masses, which have a white colour, a rose-red tarnish, and an acid, bitter taste. It is uncertain whether this substance crystallises in the mono-symmetrical or in the asymmetrical systems. Streak white, with a reddish tinge. When picro-alumogen is heated, it melts in its water of crystallisation, swells out considerably, and becomes cloudy and porous. Water dissolves it easily, the solution having an acid reaction, and depositing acute gypsum-like crystals on slow evaporation. Chemical composition as follows, viz.:—

MgO.	Al_2O_3.	SO_3.	K_2O.	CoO.	H_2O.	
8·189	9·160	36·387	0·386	trace	45·690	= 99·812

From this analysis the formula, $2MgSO_4.Al_2S_3O_{12} + 28H_2O$, is obtained, from which it appears that picroalumogen very closely resembles pickeringite ($MgSO_4.Al_2S_3O_{12} + 22H_2O$), differing only in the greater amount of magnesium sulphate and water. A very interesting fact connected with picroalumogen is its connection with related compounds: for if to a mixture of the sulphates of magnesium and aluminium a little sulphuric acid be added, and the whole allowed to evaporate spontaneously, knotty groups of prismatic crystals separate out, which proved on analysis to have a composition corresponding with the following formula, viz.: $3MgSO_4.Al_2S_3O_{12} + 36H_2O$, so that picroalumogen occupies a position between the latter compound (not yet known to occur in nature) and pickeringite. Picroalumogen is not a mechanical mixture of two sulphates, as the crystals were found to be homogeneous.

Marmatite (Zn_3FeS_4), is found crystallised in cubes, in combination with the tetrahedron, the faces of the former being rough and the latter smooth. The exterior of the crystals has a dull, brown to black colour, whilst the interior is reddish-brown, with a metallic lustre. Streak reddish, H. = 4. Spec. gr., 3·92. Found in the iron mines of Rio and Torre della Marina, in quartz.

Cerussite is found in acicular, opaque, white, lustrous prisms, sometimes 12 mm. in length, attached to limonite. Locality, Cavacce, near Rio.

Asbolite occurs enclosed in ochrey limonite, accompanied by erythrite, in the Vallone di Capo Calamita.

Orthoclase is widely distributed throughout Elba, in granite and quartz-porphyries; also particularly fine in the augitic iron-stones of Rio. Near Vigneria it occurs as adular, in talcose and chloritic quartzite, accompanied by tetrahedrons of copper-pyrites. At Rio it occurs attached to augite, and associated with ilosite. The orthoclase crystals in the quartz-porphyry of Laconella are completely changed into kaolin.

Silicate of Copper, or Chrysocolla, is found always in limonite, with other copper ores at Capo Calamita, in stalactitic forms, with knotty masses; also in crusts and deposits, but never crystallised or crystalline. It is also occasionally found on magnetic iron.

Chalcantite, ($CuSO_4+5H_2O$), always found in the iron ores at Capo Calamita, not crystallised, but as a crust or efflorescence.

Uranite is found in the island of Montecristo, in a geode of granite, situated between orthoclase; is rare in Elba.

Arsenical-pyrites (*Mispickel*).—Found in the granite of Montecristo. Massive, blue-grey. H. = 5—6.

Magnetic iron sand has lately been found delineating a granite vein, accompanied by an excess of mica, at Grotta d'Oggi, near San Piero. The upper part of the magnetic iron deposit is partially decomposed, and contains numerous black magnetite crystals, some of which exhibit a bronze-like tarnish. The crystals, which are octohedrons or rhombic dodecahedrons, or combinations of both, have a diameter of from ½ to 1 centimeter, and are strongly polar-magnetic. Lower down in the vein-stone the magnetite crystals increase in size, but are less freely crystallised. Magnetite also occurs in the green diorite slate, at Caviere, near San Piero, but it is not so strongly magnetic as that found in the granite, and not crystallised.

Limonite has been found by the author pseudomorphous, after iron-pyrites, at Facciatoria, near San Piero, in a granite geode.

Tourmaline is very widely spread throughout Elba. Foresi and the author examined a large number of specimens, and found that most of the apparently black-coloured tourmaline crystals were in reality red; for instance, 385 crystals were examined, and only 18 were found to be really black, the majority having a garnet-red or wine-red colour; a few exhibited two colours (red and green) on the same individual. On attached crystals which exhibit two colours, it appears that the green colour is nearest to the base, whilst the red colour fills up the intervening space to the terminals; the colours are, however, not sharply separated from each other into two distinct portions, but each of them occurs twice in succession alternately. One red crystal exhibited a fine green ring at its terminal.

Vesuvianite occurs in a quartz vein in the granite, near il Prato (San Piero), in clefts and in small geodes. The crystals are numerous, and closely resemble rhombic dodecahedrons in form, and were formerly mistaken for garnets. $H = 6{\cdot}5$. Spec. gr. 3·722—3·788. The prism of the first order predominates; the prism of the second order is very slightly developed, whilst the pyramid of the first order terminates the crystals. The marble of il Prato also encloses garnet and vesuvianite, the latter being characterised by a well-defined basal plane, and a striation upon $\infty P\infty$.

Thulite occurs at Campo a Peri, not freely crystallised, but in aggregations and veins on clefts in the diallagite of that district.

Opal is found as *perlite* and *fiorite*, in the neighbourhood of San Piero, in kaolin, also as a crust and globular. At Vallicella, in the same neighbourhood, opal occurs unusually pure as hyalite, in cavities, in a granite vein. The opal of Sant Ilario and San Piero encloses garnets, those of the former locality being light yellow, and those from the latter locality, black.

Barytes is found on calcite at le Serre and le Cavine, both localities being in the neighbourhood of San Piero. The crystals of barytes are tabular, varying from 5 to 25 mm. in size, and exhibit the combination, $0P.\infty P.\infty P\bar{\infty}$, accompanied by pseudomorphs of limonite after iron-pyrites, in the form of cubes, or a combination of the cube with the octohedron.

Quartz was found at Palombaia, near San Piero, in extraordinary crystals, having numerous faces; these crystals have been described by Bombicci, vom Rath, and D'Archiardi. A new locality was afterwards discovered by Celleri, at Golfo della Biodola, on the road from Portoferraio to Marciana. The quartz from Polombaia is found partially free and distributed about in the detritus of clefts and hollows in the rock, and partially in nests in a quartzite, which is either coarse-grained, pulverulent, with an ochre-yellow colour, or else massive and white. The crystals found in the detritus in the clefts are characterised by the roundness of their faces, edges, and angles, having in fact the appearance of molten glass. Again, the crystals found in the quartzite do not exhibit very marked alterations in their exterior. Similar appearances were observed on quartz crystals from the Golfo della Biodola. The author ascribes the peculiar formation of these quartz crystals to an interrupted crystallisation, and not to any chemical action.

C. A. B.

Organic Chemistry.

Distillation of Oil of Turpentine and Carbon Tetrachloride by Steam. By ALEX. NAUMANN (*Deut. Chem. Ges. Ber.*, x, 1819—1821).—The author finds, by a method of experiment already detailed (*Deut. Chem. Ges. Ber.*, x, 1421; p. 47 of this volume), that in the case of oil of turpentine, the temperature of the vapour is 1·6° above that of the liquid, and that 71 volumes of water distil over for every 100 volumes of the oil.

In the case of carbon tetrachloride, the vapour-temperature is 1·0° above that of the liquid, and for every 100 volumes of the tetrachloride, 6·6 volumes of water distil over, thus showing that the regularities observed in the distillation of liquids, such as benzene, toluene, &c., which float on water, are found to hold in case of liquids which are heavier than water.

P. P. B.

Preparation of Alcoholic Chlorides, and their Application in the Manufacture of Colouring Matters. By P. MONNET and F. REVERDIN (*Bull. Soc. Chim.* [2], xxix, 106—108).—Methyl alcohol and hydrochloric acid are heated to 100° under a pressure of 30—35 atmospheres, and the methyl chloride thus obtained is passed into an alkaline solution of methyl-violet in methyl alcohol, until the solution is saturated, when it is heated to 95° under a pressure of 4 or 5 atmospheres.

The product thus obtained is distilled with an alkali, and the solution containing methyl-green is filtered from excess of violet, and treated with a zinc salt; the double compound thus formed is decomposed with sodium chloride, which precipitates the colouring matter.

By substituting rosaniline for methyl-violet, Hofmann's violet was obtained.

The above method for the preparation of methyl chloride may be applied to the manufacture of other alcoholic chlorides.

L. T. O'S.

Action of Alcoholic Potash on Chloroform. By M. BERTHELOT (*Bull. Soc. Chim.* [2], xxix, 4—6). By acting on a solution of chloroform in absolute alcohol, with alcoholic potash, the author has obtained results which show that for the complete decomposition of 1 equivalent of chloroform, between 2 and 3 equivalents of potash are sufficient, instead of 4 equivalents, as required by theory. From this and from the fact that a portion of the chlorine does not enter into combination with the potassium, he thinks it probable that a tribasic formic ether is produced, together with a chlorinated compound. L. T. O'S.

Normal Nitrobutane. By J. ZÜBLIN (*Deut. Chem. Ges. Ber.*, x, 2083—2087).—Normal nitrobutane, $C_4H_9NO_2$, prepared by the action of silver nitrate on well cooled normal butyl iodide, is a colourless liquid, lighter than water, distilling without decomposition at 151—152°. It is a weak acid, soluble in caustic potash, and is easily converted into butylamine by the action of tin and hydrochloric acid. Butylamine hydrochloride forms a crystalline double salt with platinic chloride, and reduces alkaline solutions of copper, silver, and mercury salts.

Nitrobutane is decomposed by heating with hydrochloric acid to 140°, splitting up into hydroxylamine hydrochloride, and normal butyric acid. By the action of nitrous acid it is converted into normal butylnitrolic acid, a yellow oil, soluble in alkalis, forming a deep red solution.

Normalmonobromonitrobutane, $CH_3.CH_2.CH_2—CHBr(NO_2)$, prepared by the action of bromine on normal potassium nitrobutane, is a heavy oil, boiling at 180—181°.

The *dibromonitrobutane*, obtained by the action of bromine on a mixture of normal nitrobutane and caustic potash, is a heavy, yellow oil, insoluble in caustic potash, boiling at 203—204°.

Normal dinitrobutane.—Dilute sulphuric acid is slowly added to a mixture of potassium nitrite and normal monobromonitrobutane dissolved in excess of caustic potash, until a blue colour is produced. Caustic potash is now added, the resulting potassium dinitrobutane acidified with sulphuric acid, and the dinitrobutane extracted with ether. This substance is a yellow oil, boiling at 190°, but decomposed by distillation.

The potassium salt forms brilliant golden scales, soluble in water and in alcohol. The aqueous solution gives with silver nitrate a precipitate of silver dinitrobutane, which can be obtained by recrystallisation in large scales, which appear yellow by transmitted, and bluish-violet by reflected light.

Normal monobromodinitrobutane, $C_3H_7.CBr(NO_2)_2$, obtained by acting on potassium dinitrobutane with bromine-water, is an oily liquid which decomposes on distillation. W. C. W.

Primary Isonitrobutane. By J. ZÜBLIN (*Deut. Chem. Ges. Ber.*, 2087—2089).—*Isomonobromonitrobutane*, $(CH_3)_2CH.CHBr.(NO_2)$, is a heavy oil, boiling at 173—175°, which resembles its isomeride in its properties.

Isodinitrobutane is a yellow oil, which decomposes on distillation. Its vapour burns without explosion, and its salts are not explosive. Potassium-isodinitrobutane forms yellow needle-shaped crystals, which are readily soluble in water. Silver isodinitrobutane is deposited from a hot aqueous solution in shining needles, containing half a molecule of water of crystallisation.

Isomonobromodinitrobutane is obtained by the action of bromine-water on an aqueous solution of potassium-isodinitrobutane. The crude product is treated with sulphurous acid, to remove free bromine, and purified by washing with caustic soda, and distillation in a current of steam. The pure substance resembles camphor in appearance; it melts at 38°.

Isonitrobutylazophenyl, $C_6H_5—N=N—CH(NO_2)CH(CH_3)_2$, a yellow oil, soluble in alkalis, is prepared by mixing diazobenzene nitrate with potassium isonitrobutane. W. C. W.

Solid Dichloroproprionitril. By H. Beckurts and R. Otto (*Deut. Chem. Ges. Ber.*, x, 2040—2041).—This body appears to be a polymeric modification of liquid dichloropropionitril, as the latter, on boiling for a long time in a reversed condenser, in contact with sodium or potassium or sodium amalgam, is converted into the solid modification, melting at 73·5°. T. C.

Mode of Action of Hydrocyanic Acid. By O. Wallach (*Deut. Chem. Ges. Ber.*, x, 2120—2128).—V. Meyer considers that the conversion of chloral into dichloracetic acid, by the action of potassium cyanide, is analogous to the general phenomenon that aldehydes in alkaline solution take up the elements of water, one molecule of aldehyde being reduced, and the other oxidised. The following experiments show that this view is incorrect, and that the decomposition is brought about by the potassium cyanide in virtue of its being a cyanide, and is not due to its alkaline properties.

Very dilute solutions of caustic alkalis or alkaline carbonates split up chloral into chloroform and formic acid, and not into dichloracetic acid and potassium chloride. Even magnesium hydroxide produces the same change.

On heating chloral and hydrocyanic acid at 100° the following reaction takes place:—$CCl_3.COH + H_2O + (HCN) = CCl_2H.COOH + HCl + HCN$. Only a small quantity of dichloracetic acid is, however, obtained in practice, owing to the injurious effect of the hydrochloric acid set free during the reaction. The yield of dichloracetic acid is largely increased, by adding magnesia or magnesium carbonate to the mixture of chloral and hydrocyanic acid.

Alcoholic chloral-solution heated to 100° with anhydrous sodium acetate yields chloroform and formic acid; but on boiling an alcoholic solution of chloral hydrocyanide with sodium acetate, sodium chloride separates out and the chloral is completely converted into dichloracetic acid. The hydrocyanic acid escapes during the reaction, without having undergone any change. A very small quantity of hydrocyanic acid could, under favourable conditions, convert an unlimited amount of chloral into dichloracetic acid.

Hydrocyanic acid in presence of chloral decomposes water, the free hydrogen replacing an atom of chlorine in the chloral, and the oxygen converting the aldehyde to acid; in this way dichloracetic acid is formed.

This is analogous to the decomposition of ammonium alloxanate, in presence of hydrocyanic acid, into dialuric and parabanic acids. (Strecker, *Ann. Chem. Pharm.*, cxiii, 47.)

$$2CO(NH—CO)_2CO + H_2O = CO(NH—CO)_2CHOH + CO(NH.CO)_2 + CO_2.$$

Hydrocyanic acid has a great affinity for water, which it tends to split up into oxygen and hydrogen, but the decomposition takes place only under favourable conditions. The presence of hydrocyanic acid lessens the intensity of the affinity of hydrogen for oxygen; now if another compound which is at the same time easily oxidised and easily reduced, is brought into the aqueous solution of hydrocyanic acid, the water will be decomposed. The free hydrogen and oxygen will act only on that compound which most readily unites with them, and the other body, *e.g.*, the hydrocyanic acid, will remain unchanged. The decomposition of chloral by hydrocyanic acid is an instance of catalytic action. The conversion of pyroracemic acid into carbon dioxide and lactic acid (Böttinger, *Deut. Chem. Ges. Ber.*, ix, 1621), and the transformation of glyoxalic acid into glycollic and oxalic acids (*ibid.*, x, 1084), are also examples of the catalytic action of hydrocyanic acid.

The author considers that the physiological action of hydrocyanic acid may be due to the same cause. W. C. W.

Ethylidenimid-argentic Nitrate. By C. LIEBERMANN and A. GOLDSCHMIDT (*Deut. Chem. Ges. Ber.*, x, 2179—2181).—In the course of his investigations upon aldehyde, Liebig observed, on mixing concentrated solutions of silver nitrate and aldehyde ammonia, the formation of a white crystalline precipitate, which he found to contain ammonia, aldehyde, nitric acid and silver. While the authors' analyses of this body fully corroborate the numbers obtained by Liebig for the percentage of C, H and Ag, they have also established the percentage of N, which Liebig failed to do, being unable to prevent the formation of nitric oxide. In addition to the estimation of the total nitrogen by Dumas' method, the authors have determined the quantities of both basic and acid nitrogen. Their results are generalised by the formula $2(C_2H_4.NH).AgNO_3$. This body is regarded as an addition-compound of the hitherto unknown ethylidenimide, $C_2H_4 \equiv NH$.

C. F. C.

Theory of the Formation of Ethers of Organic Acids by means of Hydrochloric Acid. By L. HENRY (*Deut. Chem. Ges. Ber.*, x, 2041—2045).—The author considers the usual explanation (Friedel, *Compt. rend.* (1869), 68, 1557) of the formation of compound ethers by the action of hydrochloric acid on a mixture of the alcohol and organic acid as insufficient, one of his chief objections being the following:—If, as according to that theory, these ethers are produced first by the formation of an acid chloride and then by the action of the latter on the alcohol, the acid chloride formed in the first instance will find itself in presence of water and alcohol. Now from the principles of thermochemistry this acid chloride would react rather with the water than with the alcohol, for the experiments of Berthelot and

Louginine show that by the action of acid chlorides on water heat is evolved, whereas by their action on alcohols heat is absorbed.

In opposition to Friedel's theory the following is proposed:—The carboxyl of an organic acid is at the same time both an oxide and a hydroxide $\left(-\mathrm{C}\Big\langle{}^{\mathrm{O}}_{\mathrm{OH}}\right)$, and acids are therefore oxyhydroxides of a radical containing carbon, acetic acid being the oxyhydroxide of the trivalent group ethenyl, C_2H_3. Like oxides and hydroxides generally, acetic acid combines with water, and gives the trihydroxide $CH_3—C(OH)_3$, and this is the real acetic acid, for the perfectly pure acid, $C_2H_4O_2$, does not redden litmus-paper and does not attack most carbonates. Alcohols react with acids in a manner similar to water; thus, ethyl alcohol gives with acetic acid mono-ethyl-ethenyl, $CH_3—C(OH)_2(OC_2H_5)$, which may be considered as a diatomic alcohol, or glycol; by the action of hydrochloric acid this is converted into chloro-monethyl-ethenyl, $CH_3—C(OH)Cl(OC_2H_5)$; but it has been proved that (OH) and (Cl) cannot remain attached to the same carbon-atom, so that HCl is evolved and the ethyl ether of acetic acid results, thus:—$CH_3—C(OH)Cl(OC_2H_5)—HCl = CH_3—\mathrm{C}\Big\langle{}^{\mathrm{O}}_{\mathrm{OC_2H_5}}$.

T. C.

A Decomposition of Ethyl Borate. By H. Schiff (*Gazzetta chimica italiana*, vii, 356—358).—A specimen of ethyl borate kept for a long time in a moist place in an imperfectly closed vessel was in great part converted into a colourless transparent vitreous mass. It was thought at first that this might be a vitreous variety of boric acid analogous to the vitreous silicic acid formed from ethyl silicate under similar circumstances: on examination however it was found to be neither boric anhydride, nor normal boric acid, BH_3O_3, but apparently either a polyboric anhydride or a polyboric ether.

C. E. G.

Remarks on Kosmann's "Research on Glycerin, Cellulose, and Gum. Transformation of Glycerin into Glucose." By L. Liebermann (*Deut. Chem. Ges. Ber.*, x, 2095—2097).—Kosmann has recently described (*Bull. Soc. Chim.*, xxviii, 246) experiments which prove in his opinion that glycerin is converted into glucose by the action of (1) metallic iron, (2) potassium permanganate, and (3) a mixture of potassium bichromate and dilute sulphuric acid. The amount of glucose supposed to be formed was estimated by Fehling's solution.

The author points out that Kosmann's liquids contained manganous, ferrous or chromic salts, all of which possess the power of reducing an alkaline copper solution, and that if these salts are removed, the substance loses its power of reducing Fehling's reagent. This shows that no glucose was formed.

W. C. W.

Bye-Products obtained in the Preparation of Aldehydes by Piria's Method. By St. Pagliani (*Deut. Chem. Ges. Ber.*, x, 2055).—When a mixture of the lime salts of two fatty acids (one of them being formic) is subjected to dry distillation, there are formed, as the normal products, not only an aldehyde, but also the corresponding alcohol, the hydrogen required for the latter being derived from the decomposition of the formate, thus :—$C_nH_mCO_2.Ca.CO_2H + (H.CO_2)_2Ca = 2CaCO_3 + C_nH_m.CH_2.OH + CO$.

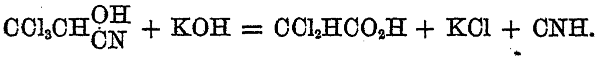
Thus a mixture of butyrate and formate gives butyric aldehyde and alcohol, together with butyrone and butyral; whilst a mixture of acetate and formate gives acet-aldehyde and ethyl-alcohol, together with acetone.

T. C.

Certain Reactions of Chloral. By O. WALLACH (*Deut. Chem. Ges. Ber.*, x, 1525—1530).—In extension of his investigation of the decomposition of chloral by potassium cyanide, the author finds that by the action of the more complicated cyanides upon this body, dichloracetic acid is likewise formed. In the case of potassium ferrocyanide, the formation of this acid is explained by the equation:—

$$2FeCy_6K_4 + 3[C_2Cl_3OH + H_2O] = 3CCl_2HCO_2K + 3KCl + 2FeCy_3K + 6CNH.$$

The resolution of chloralcyanhydrate into chloral and an alkaline cyanide, by the alkalis, results in the formation of dichloracetic acid, as a consequence of the mutual reaction of the immediate products of decomposition, thus:—



$$CCl_3CH^{OH}_{CN} + KOH = CCl_2HCO_2H + KCl + CNH.$$

The above reactions are applied by the author to the production of dichloracetic ether, for which the necessary details are given. By heating chloralcyanhydrate with alcohol for some hours at 180°, dichloracetic ether is formed: the decomposition of chloralcyanhydrate into dichloracetic acid takes place, therefore, independently of the alkalis.

The action of the cyanides upon butyl chloral the author finds to be entirely analogous to that already described. Dichlorobutyric acid appears to be formed according to the equation:—

$$C_4Cl_3H_5O + CNK + H_2O = C_4Cl_2H_6O_2 + KCl + CNH,$$

but owing to its instability passes at once into monochlorocrotonic acid. This reaction may be advantageously applied to the production of the latter acid.

That water plays a double part in decompositions of this nature, viz., of simultaneous oxidation and reduction by means of its elements, appears to be the only possible explanation of its action. The author is of opinion that the formation of mono- in place of a dichloracetanilide, by the action of aniline acetate upon chloracetylcyanide, which was observed by Pinner, may be referred to a reduction by means of hydrogen which has been liberated from water formed in the course of the reaction.

C. F. C.

A Process for Preparing Formic Acid. By V. MERZ and J. TIBIRIÇA (*Deut. Chem. Ges. Ber.*, x, 2117).—Sodium formate can be prepared by passing a stream of carbon monoxide over soda-lime heated in an oil-bath to a temperature between 200° and 250°. The absorption of carbon monoxide by soda-lime may be used as a lecture experiment to demonstrate the formation of organic compounds from inorganic materials, and it might be employed for manufacturing formic acid should a large demand for this acid ever arise.

W. C. W.

A Crystalline Compound of Bromine and Acetic Acid. Acetic Acid Dibromide. By C. HELL and O. MÜLHÄUSER (*Deut. Chem. Ges. Ber.*, x, 2102—2108).—Bromine and acetic acid in a state of purity do not act on each other at the ordinary temperature, but in presence of a very small quantity of carbon disulphide they unite together, forming needle-shaped orange-red crystals, melting at 36°, and having the composition $C_2H_4O_2.Br_2$. In presence of their mother-liquor these crystals change into thick prisms. This substance is very hygroscopic, it dissolves in chloroform and carbon disulphide without undergoing decomposition; it is also easily soluble in alcohol, ether, benzene, and in glacial acetic acid with evolution of hydrobromic acid. It dissolves in water with separation of bromine. This body is either a molecular compound of bromine and acetic acid, or it may be regarded as $(CH_3)C(Br)(OBr)(OH)$.

W. C. W.

On the Acid Acetates. By A. VILLIERS (*Compt. rend.*, lxxxv, 1234—1237).—In continuation of his researches on the acid acetates (*Chem. Soc. J.*, 1877, ii, 428) the author has prepared the acid salts of strontium, barium, copper, and manganese by dissolving the neutral acetates in varying proportions of acetic acid.

Strontium forms several hydrated acid acetates which crystallise in very definite forms; but they are unstable, efflorescing the more rapidly as the proportion of acid is increased. The relation existing between the acetic acid and the neutral acetate in the three strontium compounds which have been so prepared is as 1 : 2, 2 : 3, and 3 : 4.

Two acid acetates of barium have been obtained.

By cooling a solution of copper acetate in hot glacial acetic acid, the acid salt is obtained in brilliant green crystals, which retain the same quantity of water of crystallisation as the neutral acetate. The acid acetate of manganese is prepared in a similar manner, and consists of small granular crystals of a paler rose-colour than the neutral salt.

No acid acetate of lead has been obtained, the neutral acetate which dissolves to a very great extent in glacial acetic acid being again deposited.

A. J. C.

Preparation of Dichloropropionic from Glyceric Acid. By WERIGO and MELIKOFF (*Deut. Chem. Ges. Ber.*, x, 1499—1500).—The preparation of dichloropropionic from glyceric acid is readily accomplished, by converting the latter into chloracrylic acid, by boiling its chloranhydride with alcoholic potash, and heating the resulting acid with hydrochloric acid at 100° in sealed tubes. The melting point of dichloropropionic acid the authors find to be 50°; its ethylic ether boils at 183—184°. By the oxidation of the dichloride of allyl alcohol the authors obtain an acid melting at 50° and yielding an ethylic ether boiling at 184°. The identity of the products of the two reactions, which is sufficiently evident, is further substantiated by their both yielding a β-chloracrylic acid melting at 64—65°. C. F. C.

Action of "Molecular Silver" upon α-Dichloropropionic Acid. By H. Beckurts and R. Otto (*Deut. Chem. Ges. Ber.*, x, 1503—1504).—By the action of so-called molecular silver (1 at.) upon α-dichloropropionic acid (1 mol.), previously dissolved in benzene, an acid is obtained in large transparent quadratic crystals (m.p. 185°) which has the composition of a dichloradipic acid. This acid, whose formation may be explained by the following equation,

$$2(CH_3CCl_2.CO.OH) + 2Ag = (CH_3)Cl(COOH)C—C(CH_3)Cl(COOH) + 2AgCl,$$

is converted by the action of nascent hydrogen at ordinary temperatures into an acid which contains no chlorine; it can hardly, therefore, be regarded as a substitution-product of ordinary adipic acid. By the action of 2 at. silver upon 1 mol. α-dichloropropionic, an acid is obtained belonging presumably to the $C_nH_{2n-4}O_4$ series, and either identical or isomeric with hydromuconic acid.

The authors are engaged in a further investigation of these acids. C. F. C.

Dichloropropionic Acid (a Correction). By L. Henry (*Deut. Chem. Ges. Ber.*, x, 1854).—The author shows that the assertion made by Messrs. Werigo and Melikoff that the boiling point of the ethylic ether of dichloropropionic acid as given by the author (*Deut. Chem. Ges. Ber.*, vii, 414), is 30° too low, arises from a misprint, which was corrected in vol. vii, *Deut. Chem. Ges. Ber.* P. P. B.

α-Dichloropropionic Acid. By H. Beckurts and R. Otto (*Deut. Chem. Ges. Ber.*, x, 2037—2040).—This acid can be boiled with water under ordinary pressure without decomposition; if, however, a mixture of equal parts of the acid and water be heated to 120—150° in sealed tubes, it is converted, with evolution of hydrochloric acid, partly into pyrotartaric acid, and partly into the condensation-products of pyrotartaric acid (Böttinger, *Liebig's Annalen*, clxxxviii, 293), thus:—

$$C_3H_4Cl_2O_2 + H_2O = C_3H_4O_3 + 2HCl.$$

The authors cannot confirm the statement of Klimenko (*Deut. Chem. Ges. Ber.*, vii, 1406), that the ethylic ether of dichloropropionic acid (obtained from pyrotartaric acid) on treatment with silver oxide yields carbacetoxylic acid, previous to decomposition into carbonic and acetic acids, thus:—

$$CH_3—CCl_2—COOAg + 2Ag_2O = CH_2.OH—CO—COOAg + 2AgCl + Ag_2;$$

for they find, on repeating Klimenko's experiments, that carbonic and acetic acids are produced directly under the above circumstances without the intermediate stage of conversion into carbacetoxylic acid; and that, contrary to previous results, α-dichlorpropionic acid can be obtained in the form of crystals melting above 15°. T. C.

α-Monochloracrylic Acid from α-Dichloropropionic Acid. By H. Beckurts and R. Otto (*Deut. Chem. Ges. Ber.*, x, 1948—1953).—The authors have previously shown that monochloracrylic acid is formed by heating the silver salt of dichloropropionic acid (*Deut. Chem. Ges. Ber.*, x, 264; *Journ. Chem. Soc.*, 1877, ii, 181). In order to obtain the pure acid they proceed as follows:—Dilute dichloropropionic acid is mixed in a retort with half the number of molecules of silver carbonate, added in small portions. When the evolution of carbon dioxide has ceased, the liquid is heated to 100° for some time to complete the reaction, and afterwards distilled. The distillate passing over at 150—200°, and consisting of crude monochloracrylic acid, is dehydrated with dried cupric sulphate and re-distilled. The pure product passes over at 176—181°. It is a colourless, oily liquid, of faint peculiar odour, soluble in all proportions of water, alcohol, and ether. It volatilises at the ordinary temperature, and distils in considerable quantity with steam. When distilled *per se*, it undergoes partial decomposition, hydrochloric acid being separated. The formation and constitution of the acid are represented by the equation—

$$CH_3—CCl_2—COOAg = CH_2{=}CCl—COOH + AgCl.$$

It corresponds with the bromacrylic acid which Phillippi and Tollens obtained from α-dibromopropionic acid, and is isomeric with the acid obtained by Werigo and Werner from glyceric acid, by Pinner from trichlorolactic acid, and by Wallach and Hunäus from chloralide, which, from its constitution, $CHCl{=}CH—COOH$, may be called monochloracrylic acid.

The following salts of α-monochloracrylic acid were obtained by neutralising the crude acid with the respective bases or their carbonates, and evaporating the solutions at the ordinary temperature. At higher temperatures the salts decompose more or less easily, metallic chlorides being separated.

The *potassium salt*, $CH_2{=}CCl—COOK + H_2O$, forms tables and prisms, which dissolve very easily in water, lose their water of crystallisation at 100°, and evolve pungent vapours at higher temperatures.

The *sodium salt* crystallises with 1 mol. of water in long flat needles, which dissolve very easily in water and effloresce in the air.

The *calcium salt* $(CH_2{=}CCl—COO)_2Ca + 7H_2O$, and the *barium salt*, with 3 mols. of water, are left, on evaporation of their solutions, in the form of gelatinous masses, which are converted by addition of absolute alcohol into white crystalline powders.

The *silver salt*, $CH_2{=}CCl—COOAg$, forms small white laminæ, freely soluble in water, and very unstable even at common temperatures.

Conversion of α-Monochloracrylic into Dichloropropionic Acid.—This conversion is effected by heating α-monochloracrylic acid at 120—150° for three or four hours with hydrochloric acid in sealed tubes. The α-dichloropropionic acid thus formed boils at 186—190°. It is also formed by passing hydrogen chloride into a warm aqueous solution of chloracrylic acid:—

$$CH_2{=}CCl—COOH + HCl = CH_3—CCl_2—COOH.$$

When hydrogen chloride is passed into an alcoholic solution of α-monochloracrylic acid, the ethyl-ether of α-dichloropropionic acid is formed. This substance boils at 160°, and when shaken with aqueous ammonia yields α-dichloropropionamide, melting at 117°.

α-Monochloracrylic acid, in acid solution, is converted by the action of nascent hydrogen into propionic acid. J. R.

Methylcrotonic Acid. By W. v. MILLER (*Deut. Chem. Ges. Ber.*, x, 2036—2037).—On oxidising valeric acid with an excess of potassium permanganate, Neubauer (*Ann. Chem. Pharm.*, cvi, 62) obtained what he considered to be angelic acid. The author has repeated Neubauer's experiments, and has prepared a well crystallised substance, the analysis of which agrees with the formula of angelic acid. It appears to be methyl-crotonic acid, but melts at 69·5°, and not at 62·5° as found by Frankland and Duppa, and others. T. C.

Methylcrotonic Acid. By AUG. RÜCKER (*Deut. Chem. Ges. Ber.*, x, 1964).—Geuther has shown that when ethylic aceto-acetate is treated with phosphorus pentachloride, and the product of the reaction is thrown into water, two isomeric acids, chlorocrotonic and chlorisocrotonic, $C_4H_5ClO_2$, are formed. The author finds that ethylic methyl-aceto-acetate, when similarly treated, yields only one chlorinated methylcrotonic acid, $C_5H_7ClO_2$. This substance volatilises with water-vapour, melts at 69·5°, and sublimes in pungent vapours at a somewhat higher temperature. Its barium and sodium salts crystallise with difficulty, and deliquesce in the air. The silver salt is sparingly soluble, and but little sensitive to light. The ethyl-ether boils at 173—175°.

α-Methyl-β-oxybutric acid, obtained from ethylic methyl-aceto-acetate by Rohrbeck's reaction, is converted by heating to 110° with hydriodic acid into ordinary methylcrotonic acid melting at 62·5°.

J. R.

Distillation of Castor Oil under Reduced Pressure. By F. KRAFFT (*Deut. Chem. Ges. Ber.*, x, 2034—2036).—When castor oil is distilled under a very low pressure, there passes over, first a colourless oily distillate, equal to about $\frac{1}{3}$ or $\frac{1}{2}$ of the oil used, and then a small quantity of an oily liquid, whilst a slimy saponifiable mass remains in the retort. Half of the oily distillate consists of œnanthol, which is separated by distillation; after the œnanthol has distilled over, the temperature suddenly rises above 100°, and then remains stationary. The distillate which now comes over solidifies to a crystalline mass, the analysis of which led to the formula, $C_{11}H_{20}O_2$; this melts at 24·5°, and boils at 198—200° under a pressure of 90 mm.

It appears to be a new member of the oleic series, forming a crystalline barium salt; on fusing with potash, it gives acetic and nonylic acids; with bromine it forms a crystalline addition-product, melting at 38°. The following equation represents the formation of œnanthol, and of the new acid from ricinoleic acid: $C_{18}H_{34}O_3 = C_7H_{14}O + C_{11}H_{20}O_2$.

The remainder of the distillate obtained from the castor oil distilled under the above pressure chiefly at 250—265°, but has not yet been investigated. T. C.

Diallyl-aceto-acetic Ether and some of its Derivatives. By Carl Wolff (*Deut. Chem. Ges. Ber.*, x, 1956—1958).—Sodium dissolves in ethylic allyl-aceto-acetate, evolving hydrogen, and forming ethylic sodium-allyl-acetoacetate, thus:—

$$2[CH_3—CO—CH(C_3H_5)—CO.OC_2H_5] + Na_2$$
$$= 2[CH_3—CO—CNa(C_3H_5)—CO.OC_2H_5] + H_2.$$

This product reacts with allyl iodide or bromide to form sodium iodide or bromide and *ethylic diallyl-aceto-acetate*—

$$CH_3—CO—C(C_3H_5)_2—CO.OC_2H_5,$$

a colourless oily liquid of faint peculiar odour, boiling at 239—241°, and having the sp. gr. 0·948 at 17·5°. The diallyl-compound, like all substituted aceto-acetic ethers, is decomposed by alkalis in two ways, yielding on the one hand *diallyl-acetone*, and on the other, acetic and *diallyl-acetic acids*:—

$$CH_3—CO—C(C_3H_5)_2—CO.OC_2H_5 + 2HOK$$
$$= CH_3—CO—CH(C_3H_5)_2 + CO(OK)_2 + HO.C_2H_5;$$

$$CH_3—CO—C(C_3H_5)_2—CO.OC_2H_5 + 2HOK$$
$$= CH_3—CO.OK + CH(C_3H_5)_2—CO.OK + HO.C_2H_5.$$

Diallyl-acetone is a colourless light oily liquid of unpleasant odour, boiling at 174—175°.

Diallyl-acetic acid is an oily liquid of sp. gr. 0·9495 at 25°, boiling at 221—222°. Its sodium salt is extremely deliquescent. The barium salt is amorphous and easily soluble. The calcium salt, $(C_8H_{11}O_2)_2Ca + 2H_2O$, crystallises in laminæ, which are more soluble in cold than in hot water. The silver salt, $C_8H_{11}O_2Ag$, crystallises in brilliant scales.
J. R.

Diethyl-β-oxybutyric Acid. By Heinr. Schnapp (*Deut. Chem. Ges. Ber.*, x, 1953—1954).—Ethylic diethyl-aceto-acetate dissolved in weak spirit is readily converted, by the action of sodium-amalgam, into α-diethyl-β-oxybutyric acid, the sodium salt of which crystallises in thin laminæ with 6 mols. of water:—

$$CH_3—CO—C(C_2H_5)_2—CO.OC_2H_5 + Na_2 + 2H_2O$$
$$= CH_3—CH.OH—C(C_2H_5)_2—CO.ONa + NaOH + C_2H_5.OH.$$

The sodium salt gives by precipitation the silver salt, $C_8H_{15}AgO_3$, and the basic copper salt, $C_8H_{14}CuO_3$, both of which are sparingly soluble.

α-Diethyl-β-oxybutyric acid in the free state is a thickish liquid sparingly soluble in water. It is almost entirely resolved by heat into aldehyde and diethyl-acetic acid:

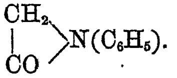
$$CH_3—CH.OH—C(C_2H_5)_2—CO.OH$$
$$= CH_3—COH + CH(C_2H_5)_2—CO.OH.$$

The latter substance boils at 195—197°, and has the sp. gr. 0·945. Its silver salt crystallises in asbestos-like needles having the formula,

$C_6H_{11}AgO$. The barium salt is crystalline and deliquescent. The ethyl-ether, $C_6H_{11}(C_2H_5)O_2$, boils at 151°. J. R.

Preliminary Notice on the Synthesis of Pimelic Acid. By A. Bauer and J. Schuler (*Deut. Chem. Ges. Ber.*, x, 2031—2033).—Neither the authors nor Guthrie (*Ann. Chem. Pharm.*, cxxi, 117) were able to obtain pimelic acid by the action of alcoholic potash on amylene dicyanide; if, however, during the action of potassium cyanide on amylene bromide, some alcoholic potash be added, potassium pimelate is produced, thus: $C_5H_{10}(CN)_2 + 2KHO + 2H_2O = C_5H_{10}(COOK)_2 + 2NH_3$. The free acid possesses all the properties ascribed by Hlasiwetz and Grabowsky (*Wien. Akad. Ber.*, lvi [2], 404) to the pimelic acid obtained from camphor. T. C.

Action of Heat on Glycocines. By Paul J. Meyer (*Deut. Chem. Ges. Ber.*, x, 1967).—Phenyl-glycocine, when heated at 140—150° for some time, loses water, and is converted into a substance which crystallises from alcohol in slender needles melting at 263,° and dissolving sparingly in hot alcohol and ether. The composition of the substance agrees with the formula—



$$\left.\begin{matrix}CH_2\\ |\\ CO\end{matrix}\right\rangle N(C_6H_5).$$

J. R.

Constitution of Chloralacetamide. Remarks on a Previous Paper. By A. Pinner (*Deut. Chem. Ges. Ber.*, x, 1964).—The author points out that the compounds of butylchloral with acetamide and benzamide recently described by Schiff and Tassinari (*Deut. Chem. Ges. Ber.*, x, 1783) were formerly described by himself (*Liebig's Annalen*, clxxix, 40). He remarks further that the constitution of chloralacetamide is represented by the formula, $CCl_3—CH(NH_2)(O.C_2H_3O)$, and not, as Schiff supposes, by the formula,

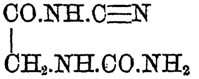
$$CCl_3—CH(OH)(NH.C_2H_3O).$$

That such is the true view of its constitution is shown by the fact that chloralacetamide is formed by the action of ammonia on chloral-acetyl chloride, which is undoubtedly represented by the formula—

$$CCl_3—CHCl(O.C_2H_3O).$$

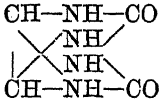
J. R.

An Acetylenecarbamide or Acetylene-urea. By A. Schiff (*Gazzetta chimica italiana*, vii, 351—356).—If a few drops of hydrochloric acid be added to a solution of glyoxal and urea, the liquid becomes warm, and in a short time deposits a mass of small white needles consisting of *acetylene-urea*, $C_4H_6N_4O_2$. When the mixed aqueous solutions are heated at 90° for a long time without the addition of acid, a substance is obtained having the same composition as above, but crystallising in minute yellow prisms; these, however, by repeated crystallisations from boiling water are converted into the colourless needles. It is uncertain as yet whether these two compounds are identical or merely isomeric. Acetylene-urea crystallises in long white needles which are only slightly soluble in ordinary solvents. Its aqueous solution gives no precipitate, either with platinum tetrachloride or gold trichloride. It does not unite with nitric or oxalic acids, and is unaltered by prolonged ebullition with baryta-water; a very concentrated solution of barium hydrate causes a deposit of barium carbonate and oxalate. When heated it is decomposed without previous fusion. Acetylenurea is isomeric with glycoluril, the compound which Rheineck prepared by the action of sodium-amalgam on allantoïn. The author expresses the relation of these two isomerides by the following formulæ:—



$$\begin{array}{l}CO.NH.C\equiv N\\ |\\ CH_2.NH.CO.NH_2\end{array}$$

Glycoluril.



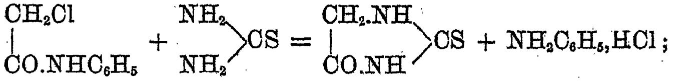
Acetylenurea.

C. E. G.

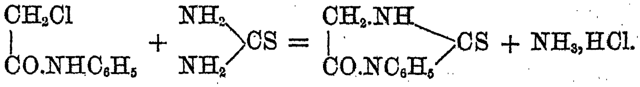
Acetylene-Carbamides. By C. Böttinger (*Deut. Chem. Ges. Ber.*, x, 1923).—Referring to Schiff's paper on this subject (see last abstract), the author states that he had previously examined the reaction of glyoxal with carbamide.

By heating a concentrated solution of glyoxal with a cold saturated solution of carbamide in 50 p.c. hydrocyanic acid, he obtained two bodies agreeing in composition with the formula, $C_4H_6N_4O_2$. One of these was precipitated in the form of a snow-white hard crystalline powder, which crystallised from hot water in long colourless needles. The other body, obtained from the mother-liquor of the first, crystallised in brilliant laminæ, the hot aqueous solution of which had an intense yellow colour. The constitution of these substances was not made out. J. R.

Substituted Thiohydantoïns. By Paul J. Meyer (*Deut. Chem. Ges. Ber.*, x, 1965—1967).—*Phenylthiohydantoïn.*—When equal numbers of molecules of chloracetanilide and thiocarbamide are dissolved in alcohol, and heated over the water-bath, thiohydantoïn is deposited in crystals, whilst the liquid contains in solution phenylthiohydantoïn, together with ammonium chloride and aniline hydrochloride. The reactions are expressed thus:—



$$\begin{array}{l}CH_2Cl\\ |\\ CO.NHC_6H_5\end{array} + \begin{array}{l}NH_2\\ NH_2\end{array}\!\!>CS = \begin{array}{l}CH_2.NH\\ |\\ CO.NH\end{array}\!\!>CS + NH_2C_6H_5,HCl;$$



$$\begin{array}{l}CH_2Cl\\ |\\ CO.NHC_6H_5\end{array} + \begin{array}{l}NH_2\\ NH_2\end{array}\!\!>CS = \begin{array}{l}CH_2.NH\\ |\\ CO.NC_6H_5\end{array}\!\!>CS + NH_3,HCl.$$

Phenylthiohydantoïn crystallises in small shining yellowish needles or prisms, which melt at 178°, and dissolve easily in hot alcohol, and in ether and acids, but not in water. It forms a crystalline sodium salt.

Toluylthiohydantoïn is obtained, together with thiohydantoïn, by the action of chloracetotoluide on thiocarbamide, in the same manner as the preceding compound. It crystallises in small, shining needles or prisms, melting at 183°, and in other respects resembles the phenyl-compound. J. R.

Propylisopropylbenzene, and Propylbenzoic and Homoterephthalic Acids. By E. PATERNÒ and P. SPICA (*Gazzetta chimica italiana*, vii, 361—366).—The authors have already given a short account of the preparation of this hydrocarbon by the action of zinc ethyl on cumyl chloride, prepared from pure cuminic alcohol (this *Journal*, 1877, i, 77); 220 grams of the chloride yielded only 20 of the pure hydrocarbon, and as this quantity was too small to make a careful examination of its derivatives, the authors directed their attention to the products of oxidation formed by treating it with very dilute nitric acid. Two acids were formed, which were separated by means of benzene, and the soluble one purified by crystallisation from ether and alcohol. It crystallises in colourless needles, which melt at 138—139°, whilst cuminic acid melts at 114—115°. The analysis corresponded closely with the formula of *propylbenzoic acid*. The *barium salt* $[C_6H_4(C_3H_7)COO]_2Ba + 2H_2O$, forms colourless, micaceous plates, and the *argentic salt*, $C_6H_4(C_3H_7)COOAg$, is a white, caseous precipitate. The second acid, which is insoluble in benzene, forms a white powder, almost insoluble in ordinary solvents, but readily soluble in alkaline solutions. It seems to be *homoterephthalic acid*,

$$COOH.C_6H_4.CH_2.COOH.$$

Its *barium salt*, $C_9H_6BaO_4$, crystallises in microscopic, rectangular plates. The silver salt is pulverulent, colourless, and but little altered by exposure to light. C. E. G.

On the Rotary Power of Metastyrolene. By BERTHELOT (*Compt. rend.*, lxxxv, 1191—1193).—Pure styrolene possesses a left-handed rotary power, in which $\alpha_D = -3.4°$. At the ordinary temperature styrolene is gradually transformed into an amorphous polymeride, metastyrolene. The opaqueness of this body has hitherto prevented the determination of its optical properties, but some of the pure styrolene, which had been prepared twelve years before (*Ann. Chim. Phys.* 4th series, xii, 159; and 5th series, ix, 53) was found to be a meta-styrolene, which was quite transparent and vitreous. The optical examination of this specimen gave $\alpha_D = -2.2°$.

Another specimen of meta-styrolene, which was in a pasty condition, from the presence of a very small quantity of unaltered styrolene, gave $\alpha_D = -2.5°$. It is not maintained that these numbers possess an absolute value; but they show the existence of the rotary power, and prove that the original sign of styrolene is retained in its polymeride, in the same manner as meta-terebenthene participates in the rotary power of terebenthene.

The permanence of the rotary power in the carbon derivative, which has been obtained in so simple a manner, would be a sufficient proof of the existence of this property in the original carbon compound, if direct evidence were impossible.

The fact of styrolene possessing rotary power condemns the theory which regards as impossible the existence of a rotary power in so simple a carbon-compound. A. J. C.

Oxidation of Nitrogenous Compounds by Potassium Permanganate. By S. HOOGEWERFF and W. A. VAN DORP (*Deut. Chem. Ges. Ber.*, x, 1936—1939).—The authors have examined the action of potassium permanganate in alkaline solution on aniline, toluidine, and quinine. Their experiments consisted in heating over the water-bath a 10 per cent. solution of potash containing the substance to be oxidised, and adding thereto in small portions a 4 per cent. solution of permanganate, so long as the liquid continued to become decolorised after each addition. The ammonia evolved was absorbed by hydrochloric acid of known strength, and estimated by titration.

Aniline thus treated gave off about half its nitrogen in the form of ammonia, whilst nearly one-third of the nitrogen remained in the liquid in the form of azobenzene, together with nitrites and nitrates, an unknown nitrogenous substance, and oxalic acid.

Toluidine gave similar results.

Quinine similarly treated gave off nearly half its nitrogen in the form of ammonia. Amongst the other products was a nitrogenised acid, which has not yet been examined.

It was found by direct experiment that neither ammonia nor azobenzene is oxidised by permanganate under the conditions of the experiments. J. R.

Action of Sulphurous Chloride and Ethyl Sulphuric Chloride on Aniline and Anilides. By LUDWIG WENGHÖFFER (*J. pr. Chem.* [2], xvi, 448—466).—Sulphurous chloride acts on aniline in a manner differing from that of the analogously constituted carbonyl chloride, producing chloro-derivatives, whilst ethylsulphuric chloride produces by its action bodies which contain the sulphuryl group.

When small quantities of an ethereal solution of aniline are added to well cooled sulphurous chloride, a violent reaction takes place, attended with the evolution of sulphurous anhydride and hydrochloric acid gas. From the solid residue left at the end of the reaction, by extraction with alcohol and sublimation of the crystals from the alcoholic solution, trichloraniline was obtained, crystallising in long, white, shining needles, melting at 80°. It is identical with the trichloraniline of Beilstein and Kurbatow (*Deut. Chem. Ges. Ber.*, viii, 1657—1684), and is isomeric with that of Lesimple (*Ann. Chem. Pharm.*, cxxxvii, 125), which melts at 96·5°. Both these trichloranilines yield by the diazo-reaction the same trichlorbenzene, melting at 63—64°, crystallising from alcohol in long transparent needles, and in which the chlorine-atoms have the positions 1.3.5. Thus the reaction of sulphurous chloride on aniline is expressed as follows:—

$$C_6H_5NH_2 + 3SO_2Cl_2 = C_6H_2Cl_3NH_2 + 3SO_2 + 3HCl.$$

Ethylsulphuric chloride prepared according to Behrend's method (*J. pr. Chem.* [2], xv, 23), was added slowly to well cooled aniline. The product washed with alcohol, and crystallised from hot water, gave rhombic plates, which become brown on exposure to air, and lose weight when heated to 110°, decomposing at 215°, with loss of sulphurous anhydride. Analysis and its general properties show it to be sulphanilic acid, $C_6H_4\left\{\begin{matrix}NH_2\\SO_2.OH\end{matrix}\right.$; with caustic potash it forms a potassium salt, $C_6H_4\left\{\begin{matrix}NH_2\\SO_2OK\end{matrix}\right.$. Treated with bromine water it yields tribromaniline, which reaction, according to Schmitt (*Ann. Chem. Pharm.*, cxx, 129), affords a distinction between sulphanilic acid and its isomeride, amidobenzenesulphonic acid.

A nearer examination of the product of the action of ethylsulphuric chloride on aniline, showed that ethyl chloride is formed, so that the reaction may be expressed as follows :—

$$C_6H_5NH_2 + SO_2{}^{Cl}_{OC_2H_5} = C_6H_4{<}^{NH_2}_{SO_2OH} + C_2H_5Cl.$$

The reaction of sulphurous chloride on acetanilide is attended with evolution of sulphurous anhydride and hydrochloric acid gas. The products, after washing with water, gave, on crystallising from ether, large white, rhombohedral crystals and smaller needles; the latter were separated from the former, partly mechanically, and partly by their greater solubility in ether. The body crystallising in rhombohedrons is a dichloracetanilide, which is easily soluble in alcohol and ether, and difficultly soluble in hot water; it melts at 143°. The melting point shows it to be identical with the dichloracetanilide of Beilstein and Kurbatow (*op. cit.*), Witt giving 140° as the melting point of the same body (*Jahresber.*, 1874, 724). By boiling with caustic potash it yields dichloraniline.

The body crystallising in needles is a monochloraniline, and melts at 162°, which shows it to be identical with that of Witt (*Deut. Chem. Ges. Ber.*, viii, 1226).

Pure ethylsulphuric chloride does not appear to act on acetanilides; if, however, it has stood for some time, and begun to turn brown, it then reacts on acetanilide, especially if warmed, a small quantity of gas being set free. The product dissolved in alcohol, and precipitated from this solution by water, gave on crystallising from ether, massive, stellate groups of white needles. Analysis showed it to have the formula, $C_6H_{16}N_2SO_4$; the reaction is, therefore, as follows :—

$$2(C_6H_5.NHC_2H_3O) + SO_2\left\{\begin{matrix}Cl\\OC_2H_6\end{matrix}\right. = C_{16}H_{16}N_2SO_4 + HCl + C_2H_6O.$$

This body, when oxidised by sulphuric acid and manganese dioxide, yields quinone (1 : 4), showing that here, as with aniline, the sulphuryl group is attached to the benzene group; demonstrating the probability of the constitution, $SO_2(C_6H_4.NH.C_2H_3O)_2$, analogous to that of the compound which Michler obtained by the action of carbonyl chloride on dimethylaniline, viz., $CO[C_6H_4.N(CH_3)_2]_2$ (*Deut. Chem. Ges. Ber.*, ix, 717).

The action of sulphurous chloride on dimethylaniline is somewhat violent, and yields a small quantity of a body, which appears to be a dichlorodimethylaniline, $C_6H_3Cl_2N(CH_3)_2$.

Ethylsulphuric chloride acts with considerable violence on dimethylaniline; and the aqueous solution of the product treated with water, neutralised with strontium carbonate, and evaporated, yielded a crystalline mass, from which strontium chloride was removed by washing with alcohol. The residue when crystallised from water yielded slender needles, having the composition, $\left[C_6H_4\left\{\begin{matrix}N(CH_3)_2\\SO_2O\end{matrix}\right.\right]_2Sr$; and from this the free dimethylsulphanilic acid was obtained, which crystallises in plates, and forms an insoluble ammonium salt. P. P. B.

Dichloranilines. By F. Beilstein and A. Kurbatow (*Deut. Chem. Ges. Ber.*, x, 2089—2091).—Of the six possible isomerides of dichloraniline, $C_6H_3Cl_2.NH_2$, three are known, viz., (1) para $Cl : Cl : NH_2 = 3 : 6 : 1$; m. p. 50°, b. p. 251°, derived from paradichlorobenzene; (2) ordinary dichloraniline (2 : 4 : 1), m. p. 63°, b. p. 245°; and (3) symmetrical dichloraniline (3 : 5 : 1), m. p. 50·5°, the two latter anilines being derived from metadichlorobenzene. The authors have succeeded in preparing the two amido-derivatives of orthodichlorobenzene. *Orthodichloraniline* (3 : 4 : 1) is obtained by chlorinating a solution of acetometachloranilide in 90 per cent. acetic acid, decomposing the chlorinated anilides with caustic soda, and distilling the free bases with sulphuric acid. The portion of the distillate boiling at 250—260° deposits crystals of paradichloraniline, m. p. 50°. On adding caustic soda to the contents of the retort, orthodichloraniline distils over. This substance, which can also be obtained by reducing nitro-orthodichlorobenzene ($Cl : Cl : NO_2 = 3 : 4 : 1$), is deposited from solution in petroleum ether, in long, shining needles, soluble in dilute hydrochloric acid, melting at 71·5°, and boiling at 272°. It is a moderately strong base. The acetyl derivative, $C_6H_3Cl_2.N(C_2H_3O)H$, crystallises from 50 per cent. acetic acid in small needles, melting at 120·5°.

This dichloraniline forms a diazo-compound, which yields ordinary unsymmetrical trichlorbenzene.

Orthodichloraniline (3 : 2 : 1).—In preparing metachlornitrobenzene, by acting on nitrobenzene with chlorine in presence of antimony pentachloride, a considerable quantity of a liquid boiling between 250° and 270° was obtained, which on reduction by tin and hydrochloric acid, yielded a mixture of ortho- and para-dichloraniline hydrochlorides. On placing the purified free bases in a freezing mixture, paradichloraniline separated out. The oily liquid, dissolved in hot dilute hydrochloric acid, deposits crystals of the new orthodichloraniline hydrochloride on cooling. The pure free base melts at 23—24°, and boils at 252°; the liquid on cooling forms large prisms, soluble in alcohol and in acetic acid, but soluble with difficulty in petroleum ether. The acetyl derivative, $C_6H_3Cl_2.N(C_2H_3O)H$, crystallises in long needles, m. p. 156—157°, soluble in alcohol, but only slightly soluble in benzene, acetic acid, and petroleum ether. The diazo-compound derived from this dichloraniline yields the trichlorobenzene (1 : 2 : 3). W. C. W.

Derivatives of Dimethylaniline. By W. Michler and A. Gradmann (*Deut. Chem. Ges. Ber.*, x, 2078—2081).—*Dimethyl-phenyl-*

benzyl-ammonium chloride, $N(C_6H_5)(CH_3)_2(CH_2.C_6H_5)Cl + H_2O$, obtained by mixing benzyl chloride and dimethylaniline in equivalent proportions at the ordinary temperature, forms tabular crystals melting at 110°, easily soluble in water and in alcohol, but are insoluble in ether. The solution of this substance gives with platinic chloride a light yellow pulverulent precipitate containing two molecules of the ammonium chloride to one of platinic chloride; it also forms a precipitate with silver nitrate. Dimethyl-phenyl-benzyl-ammonium chloride splits up into benzyl chloride and dimethylaniline on distillation, but by heating at 220—230° in sealed tubes, it is converted into a mixture of chlorides of several bases. When caustic soda is added to the aqueous solution of the crude product, an oily liquid boiling at 335° separates out. It dissolves in hydrochloric acid, and this solution forms with platinic chloride an oily precipitate, which soon solidifies. Whether the constitution of the base contained in the platinum salt is—

$$N(C_6H_4.CH_2.C_6H_5)(CH_3)_2 \text{ or } N(C_6H_4.CH_3)(CH_2.C_6H_5)(CH_3),$$

has not been decided.

Dimethyl-phenyl-benzyl-ammonium chloride is not decomposed by moist silver oxide. In order to prepare the free base, it is therefore necessary to act on the ammonium chloride with silver sulphate, and to decompose the sulphate thus obtained with baryta-water. The free base is a thick syrupy liquid, which could not be crystallised; on exposure to the air, it absorbs carbonic acid. Its aqueous solution has a strongly alkaline reaction, and precipitates iron, copper, and lead salts as hydrated oxides. On distillation the base splits up into benzyl alcohol and dimethylaniline.

$$N(C_6H_5)(CH_3)_2(CH_2.C_6H_5)(OH) = C_6H_5.CH_2OH + C_6H_5N(CH_3)_2.$$

W. C. W.

Met-azotoluene. By J. Barsylowsky (*Deut. Chem. Ges. Ber.*, x, 2097—2098).—This substance is obtained by the action of zinc dust and caustic potash on an alcoholic solution of meta-nitrotoluene. It dissolves readily in alcohol, and is deposited from this solution in large orange-red crystals, melting at 54° (orth-azotoluene melts at 137°, and par-azotoluene melts at 144°).

The azo-compound melting at 244—245°, obtained by the oxidation of para-toluidine with potassium permanganate (this *Journal*, xxvii, 273), which the author formerly considered to be meta-azotoluene, must possess a larger molecular weight and a more complicated constitution than $C_{14}H_{14}N_2$. W. C. W.

Tetraphenylmelamine. By A. W. Hofmann (*Berl. Monatsb.*, 1877, 403; *Chem. Centr.*, 1877, 738).—In an investigation published in the *Centralblatt*, 1850, p. 466, the author described a resin obtained by heating melaniline to 170°, aniline and ammonia being evolved. He then supposed this resin to be formed by the equation—

$$3C_{13}H_{13}N_3 - 2C_6H_7N = C_{27}H_{25}N_7.$$

He subsequently found that it was also formed by removing sulphur from diphenylsulphurea, in presence of ammonia. On heating this substance to a somewhat higher temperature, it crystallises after a long time; its tendency to crystallise is increased by dissolving it in alcohol and precipitating with water several times, or by dissolving in hydrochloric acid and precipitating with an alkali. It crystallises from alcohol in needles which are sparingly soluble in ether, and insoluble in water. It melts at 217°. Its formula was found to be $C_{27}H_{22}N_6$, and it is to be viewed as tetraphenyl-melamine—

$$C_3H_2(C_6H_5)_4N_6.$$

The *hydrochloride*, $C_{27}H_{22}N_6.HCl$, crystallises from alcohol in long white rhombic prisms; it is sparingly soluble in water. It forms a crystalline *platinochloride*, and a difficultly soluble *nitrate* crystallising in slender needles.

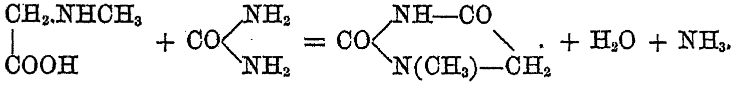
Triphenylmelaniline, when boiled with hydrochloric acid, decomposes into ammonia and phenyl cyanurate—

$$C_3H_3(C_6H_5)_3N_6 + 3H_2O = C_3(C_6H_5)_3N_3O_3 + 3NH_3;$$

but tetraphenylmelamine undergoes no change, thus indicating a difference in constitution.

Ditolylguanidine was also prepared by removing sulphur from ditolylthiocarbamide (ditolylsulphurea). It crystallises in slender needles, and melts at 168°; it is evidently identical with the base which W. Wilson obtained by acting on solid toluidine with cyanogen chloride. Ditolylguanidine behaves under the influence of heat like diphenylguanidine; a resin is formed, which, on application of more heat, gradually becomes crystalline, and is most probably *tetratolylmelamine*, $C_3H_2(C_7H_7)_4N_6$. Its hydrochloride crystallises in concentrically grouped needles. W. R.

Aromatic Hydantoïns. By P. Schwebel (*Deut. Chem. Ges. Ber.*, x, 2045—2050).—It is well known that when a mixture of sarcosine and urea is fused, methyl hydantoïn is produced—



$$\begin{array}{l}CH_2.NHCH_3\\ |\\ COOH\end{array} + CO\left\langle\begin{array}{l}NH_2\\ \\ NH_2\end{array}\right. = CO\left\langle\begin{array}{l}NH—CO\\ \qquad\diagdown\\ N(CH_3)—CH_2\end{array}\right. + H_2O + NH_3.$$

By this process the author has obtained a hydantoïn containing the group (C_6H_5) in place of CH_3.

Phenylhydantoïn.—Formed as a crystalline mass of slender needles on fusing together equivalent quantities of phenylglycocine and urea at a temperature of 155°. It melts at 191°; on long boiling, it dissolves in water and in alcohol, but is only difficultly soluble in cold alcohol, and still less in cold water. It dissolves in alkalis, and is reprecipitated by acids. In ammoniacal solution it gives white precipitates with silver nitrate and barium chloride. It dissolves neither freshly precipitated oxide of silver nor oxide of mercury; its aqueous solution does not show these reactions.

Phenylhydantoïc Acid.—The author was unable to prepare this body, though several methods were tried.

Tolyl-glycocine, $C_7H_7(HN{-}CH_2{-}COOH$.—Meyer's attempts to obtain this substance in a state of purity were unsuccessful (*Deut. Chem. Ges. Ber.*, viii, 1158). The author finds that when two molecules of paratoluidine and one of monochloracetic acid, both dissolved in ether, are mixed, and the crystalline mass produced is heated with water for some hours, then paratolylglycocine is obtained on evaporation in long slender needles. It melts at 167° with decomposition, and gives with copper sulphate a green coloration, like phenylglycocine; dissolved in concentrated hydrochloric acid, it gives with platinic chloride a yellow crystalline precipitate. By the action of mercuric chloride and stannous chloride at a boiling heat, precipitates are formed like those produced by phenylglycocine, with which latter the compound agrees in all respects, except in the ease with which it can be crystallised, and its sparing solubility in water. T. C.

On Certain Hydrazine-compounds. By EMIL FISCHER (*Liebig's Annalen*, cxc, 67—183).—The nomenclature adopted by the author for the designation of the hydrazine compounds consists of modifications of the terms employed for the bases of the ammonia type: for amine, amide, and ammonium he substitutes azine, azide, and azonium; derivatives of the class of ureas are termed carbazides, thiocarbazides, &c.; bodies containing an amide and an azide group are designated in addition by the syllable 'semi.'

Phenylhydrazine.—This body is obtained by reduction, from diazobenzene; most readily by employing the latter in the form of its compounds with the alkaline sulphites. These have, therefore, been investigated by the author.

It is clearly shown that the apparent discrepancy between the statements of Schmitt and Glutz (*Ber.*, ii, 51) on the one hand, and of Strecker and Römer (*Ber.*, iv, 784) on the other, respecting these compounds is to be attributed to the incompleteness of their investigations. By the action of diazophenol upon $KHSO_3$ the former chemists had obtained the salt, $C_6H_4(OH).N_2SO_3K + H_2O$; the latter, by acting upon diazobenzene with $KHSO_3$, obtained a salt of the composition $C_6H_5.N_2H_2SO_3K + H_2O$; belonging therefore to a class of compounds distinguished from that of which the first-named is a member, by the characteristic difference of 2 at. H. The author has complemented and reconciled these results by the following observations. By adding diazobenzene nitrate to a cold neutral solution of potassium sulphite, a solid crystalline mass is obtained, which when purified and dried over sulphuric acid, proves to be the compound $C_6H_5.N_2.SO_3K$. If, however, the acid be substituted for the neutral sulphite and the temperature allowed to rise to 25°, the salt, $C_6H_5.N_2.H_2.SO_3K + H_2O$, described by Strecker, is obtained.

That this compound is in effect a reduction-product of potassium diazobenzenesulphonate, the first-named body, is proved by acting upon the solutions of the latter with zinc-dust and acetic acid, which readily convert it into the second salt—potassium phenylhydrazinesulphonate. This body undergoes a remarkable decomposition when its aqueous solution is boiled with hydrochloric acid; the sulpho-group is eliminated as sulphuric acid, and the hydrochloride of phenylhydrazine is formed, thus:—

$$C_6H_5.N_2H_2SO_3K + H_2O + HCl = C_6H_5.N_2H_3.HCl + KHSO_4.$$

By adding diazobenzenesulphonic acid to a slightly alkaline solution of K_2SO_3, saturating with hydrochloric acid gas, and boiling the solution, a copious separation of the crystalline hydrazinebenzenesulphonic acid, described by Strecker and Römer, occurs. The reactions by which it is formed are expressed by the equations:—

(1.) $C_6H_4.N_2.SO_3 + K_2SO_3 = C_6H_4.SO_3K.N_2.SO_3K.$

(2.) $C_6H_4.SO_3K.N_2.SO_3K + K_2SO_3 + H_2O = C_6H_4.SO_3K.N_2H_2.SO_3K + K_2SO_4.$

(3.) $C_6H_4.SO_3K.N_2H_2.SO_3K + HCl + H_2O = C_6H_4.SO_3H.N_2H_3 + KCl + KHSO_4.$

Diazodibromobenzenesulphonic acid is similarly decomposed. The decomposition expressed by equation (3) is entirely analogous to that already cited as giving rise to phenylhydrazine. This compound is further formed by the reduction of the diazoamido-compounds. The decomposition of diazoamidobenzene may be represented as typical:

$$C_6H_5N.N.NH.C_6H_5 + 2H_2 = C_6H_5.N_2H_3 + H_2N.C_6H_5.$$

An important aspect of this class of decompositions is the direct conversion of the diazo- into the hydrazine-group, more especially as bearing upon the formation of hydrazine-derivatives from bodies such as naphthylamine, orthophenylenediamine, and other aromatic amines, the ordinary diazo-salts of which are either unknown, or less readily obtained than their diazo-amido-compounds.

For the preparation of phenylhydrazine in quantity, the author recommends the conversion of aniline into diazobenzene chloride, and the decomposition of the latter body by neutral sodium sulphite, according to the equation:—

$$C_6H_5.N_2.Cl + 2Na_2SO_3 + H_2O = C_6H_5.N_2H_2.SO_3Na + NaCl + Na_2SO_4.$$

The resulting sodium phenylhydrazinesulphonate is decomposed by hydrochloric acid, and finally the phenylhydrazine is isolated from its hydrochloride by treatment with caustic soda.

The necessary details are given with great exactness. The yield amounts to 70 per cent. of the theoretical.

Phenylhydrazine is a nearly colourless oil, of sp. gr. 1·091 at 21°, and boiling at 233—234°; on exposure to cold it solidifies to a crystalline mass of shining tables, which melt at 23°. It is somewhat soluble in hot water, but almost insoluble in concentrated solutions of the alkalis: it is miscible in all proportions with alcohol, ether, benzene, and chloroform. In presence of reducing agents it is exceedingly stable, but is very readily decomposed by oxidants: it reduces Fehling's solution even when in cold dilute solution, and this reaction, by reason of its delicacy, is recommended for the discrimination of all primary hydrazines, and indirectly of diazo-compounds. Phenylhydrazine is a monacid base, yielding well defined crystalline salts, of which the following are described:—

Hydrochloride, $C_6H_5.N_2H_3.HCl$.—A colourless salt crystallising in shining plates, which may be sublimed unchanged. It is precipitated from its aqueous solution by concentrated hydrochloric acid. Under no conditions could the hydrazine molecule be made to unite with 2 mol. HCl, which is additional proof of the weakening effect of the (C_6H_5)-group upon the basicity of the (NH_2)-group.

Sulphate $(C_6H_5.N_2H_3)_2H_2SO_4$ and *Nitrate*.—Both these occur in the form of white shining plates, which are easily soluble in water.

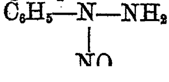
Carbazotate, $C_6H_5.N_2H_3.OH.C_6H_2(NO_2)_3$.—Crystallises in slender yellow needles.

Oxalate, $(C_6H_5.N_2H_3)_2H_2C_2O_4$.—Crystallises in colourless plates.

From numerous considerations, and especially from the synthesis of the secondary hydrazine bases, the author assigns to phenylhydrazine the constitution, $C_6H_5—NH—NH_2$: this view is in harmony with Strecker's representation of the diazo-compounds. It is much strengthened by the following observation: by the action of ethyl bromide upon phenylhydrazine, an ammonium compound of the formula, $C_6H_5.N_2H_2.(C_2H_5).C_2H_5Br$, is formed; and since the same body results from the direct addition of C_2H_5Br to ethylphenylhydrazine, and the latter body, from the mode of its formation from ethylaniline, cannot but be regarded as, $\left.\begin{matrix}C_6H_5\\C_2H_5\end{matrix}\right\}N—NH_2$, the presence of the $=N—NH_2$ group in phenylhydrazine is established. It will be further found that none of the reactions or derivatives of the base about to be discussed, in any way contravene this view.

Referred to the ammonia type, phenylhydrazine appears therefore as at once a primary and a secondary base. The presence of the NH-group is characterised by the behaviour of this body to nitrous acid and to ethyl bromide, while its more strictly basic properties appear to be determined by its NH_2 constituent. From aniline, which is its nearest relative among the amine bases, it differs in the ease with which it undergoes oxidation, by reason of which the preparation of its halogen and nitro-derivatives must be effected through the corresponding aniline compounds.

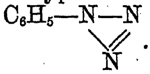
Phenylnitrosohydrazine.—By the action of sodium nitrite upon the aqueous solution of the hydrochloride of the base a compound of the formula, $C_6H_5.N_2H_2.NO$, is obtained, crystallising in yellowish plates.

This body is practically permanent in the air, but in closed vessels is rapidly converted into a dark-brown, strongly smelling liquid: this decomposition is referred to the action of minute traces of the oxides of nitrogen, which are in this way prevented from escaping. In its reactions it exhibits considerable differences from the aromatic nitroso-bodies, in which the hydrogen of the benzene nucleus is replaced by the NO-group, so that there can be no doubt that in this case the NO-molecule is in union with the nitrogen of the hydrazine group. Further, by the action of reducing agents it yields aniline in some quantity. These facts, in conjunction with the observation of Heintz, that the formation of nitrosamines from amine bases is peculiar to, and determined by the NH-group, indicate the structure of this compound to be the following:  $\begin{matrix}C_6H_5—N—NH_2\\ \quad\ \ |\\ \quad\ \ NO\end{matrix}$. This view is strongly supported by the fact that those secondary aromatic hydrazines in which the hydrogen of the NH-group is replaced by an alcohol-radicle, are decomposed by nitrous acid in a manner totally different from that here considered.

By the action of dilute alkalis, phenylnitrosohydrazine is directly resolved into the diazobenzimide of Griess, according to the equation—

$$C_6H_5.N_2H_2.NO = C_6H_5.N_3 + H_2O.$$

Since the elimination of water from nitrosamines takes place undoubtedly between the NO- and NH_2-groups, this reaction affords strong evidence in favour of Kekulé's hypothetical representation of the structure of diazobenzimide, viz.,



$C_6H_5—N—N$, $\diagdown\!\!/\!\!/$ N .

The author takes advantage of this reaction for the preparation of the latter compound, for which he gives the necessary details.

Action of Diazobenzene upon Phenylhydrazine.—The author's attempts to prepare, by means of this reaction, bodies corresponding with the so-called diazobenzamides, gave in all cases negative results. By mixing aqueous solutions of diazobenzene nitrate and phenylhydrazine chloride, diazobenzimide is separated, and the equivalent quantity of aniline obtained in solution. This, with other considerations, is explanatory of the analogous decomposition of hydrazinebenzoic acid by diazobenzene nitrate, with formation of diazobenzimide and amidobenzoic acid, in addition to aniline and diazobenzoic imide. The formation of the latter compound is referred by the author to a regeneration of aniline and nitrous acid by the resumption of 2 mol. H_2O by the diazobenzene, and the action of the nitrous acid thus formed upon hydrazinebenzoic acid, thus:—

1.) $C_6H_5.N_2.NO_3 + 2H_2O = C_6H_5.NH_2,HNO_3 + HNO_2.$
2.) $C_7H_8N_2O_2 + HNO_2 = C_7H_5N_3O_2 + 2H_2O.$

The simultaneous formation of amidobenzoic acid and diazobenzimide is explained by the equations:—

(3.) $R.NH—NH_2 + H_2O = R.NH_2 + NH_2.OH.$
(4.) $C_6H_5.N_2.NO_3 + NH_2OH = C_6H_5.N_3 + HNO_3 + H_2O.$

Equation (4) has been verified by direct experiment: by mixing aqueous solutions of diazobenzene sulphate and hydroxylamine chloride, and adding sodium carbonate to the mixture, diazobenzimide is separated in quantity approaching the theoretical.

For the conversion of hydrazine- into diazo-compounds, two methods are given: (1.) The hydrazine base is converted into its sulphonate by heating it with potassium bisulphate. Thus in the case of phenylhydrazine:—

$$4C_6H_5N_2H_3 + 2K_2S_2O_7 = 2(C_6H_5.N_2H_2.SO_3K) + K_2SO_4 \\ + (C_6H_5.N_2H_4)_2SO_4.$$

The hydrazine sulphonate is isolated, and its aqueous solution treated with mercuric oxide or potassium bichromate, by either of which it is completely oxidised to the yellow potassium diazosulphonate.

(2.) In the case of hydrazine sulphate, chloride, and similar salts, special precautions must be observed in order to prevent the occurrence of a secondary action between diazobenzene and the hydrazine base. The aqueous solution of the salt is gradually added to water holding mercuric oxide in suspension, care being taken to keep the latter in excess, and to agitate the whole continuously. In this way the following equation is to a large extent realised:

$$(R.N_2H_4)_2.SO_4 + 2O_2 = (R.N_2)_2SO_4 + 4H_2O.$$

The relations thus shown to exist between the typical representatives of the hydrazine- and diazo-groups of compounds, undoubtedly go to substantiate Kekulé's as opposed to Strecker's view of the constitution of the diazo-compounds.

The oxidation of phenylhydrazine in alkaline solution (Fehling's solution) differs essentially from that described as occurring in presence of acids: aniline and benzene are formed, with evolution of nitrogen gas.

The formation of aniline may be explained by a resolution of the hydrazine group in the manner expressed by the equation:—

$$2(C_6H_5.NH.NH_2) + O = 2(C_6H_5.NH_2) + H_2O + N_2,$$

while that of benzene is probably referable to the reduction of a diazo compound, with the entire elimination of its nitrogen and the addition of 1 at. H.

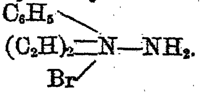
Phenylhydrazine and Ethyl Bromide.—From the product of the reaction of these bodies, after the removal of certain volatile bases by treatment with ether, water dissolves a compound which is precipitated in the form of fine white needles on adding caustic soda. This body crystallises from its alcoholic solution in transparent prisms, the composition of which is expressed by the formula—

$$C_6H_5.N_2H_2.C_2H_5.C_2H_5Br.$$

By the action of silver oxide, this compound is converted into an easily soluble alkaline hydroxide. The corresponding chloride yields a platinochloride, $\{C_6H_5.N_2H_2.(C_2H_5)_2Cl\}_2PtCl_4$.

These compounds must therefore be referred to the ammonium type, and are designated by the common prefix *phenyldiethylazonium*. While the existence of this base appears to throw doubt upon the universality of Hofmann's conclusion that the formation of ammonium compounds from amines occurs only after the entire replacement of their typical hydrogen by alcohol radicles, it is nevertheless reconciled with this view by supposing the addition of ethyl bromide to the original imide-group, the hydrogen of which has been previously replaced by ethyl. That this is, indeed, actually the case has been proved by the production of this same compound from the action of ethyl bromide upon ethylphenylhydrazine.

The construction of phenyldiethylazonium bromide is therefore represented by the formula:



$$\begin{array}{l}\quad C_6H_5\diagdown \\ (C_2H)_2 = N - NH_2. \\ \qquad Br\diagup\end{array}$$

Hence we may conclude that the formation of an ammonium compound, while it indicates the presence of a tertiary amine group in the body under experiment, is no criterion of the number of hydrogen atoms which it may contain in union with nitrogen, but that an ammonium compound may contain imide or amide groups yet intact.*

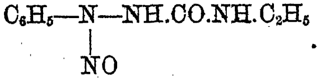
Carbamide Derivatives of Phenylhydrazine are formed by reactions precisely similar to those which are characteristic of ammonia and the amine bases. They are differentiated from ordinary carbamides by the presence of the hydrazine group: this is especially seen in their reactions with nitrous acid, and the peculiar decomposition of the thioderivatives by alkalis.

Ethylphenyl-semi-carbazide, $C_6H_5.N_2H_2.CO.NH.C_2H_5$, is formed by the direct union of phenylhydrazine and isocyanic ether. From its solution in hot alcohol it crystallises in colourless plates, which melt at 151°. Heated with concentrated hydrochloric acid at 100°, it undergoes a simple resolution into carbonic acid, ethylamine and phenylhydrazine.

By the action of nitrous acid this body undergoes a remarkable conversion into a nitroso-derivative, which is obtained in fine yellow needles, having the empirical composition, $C_9H_{12}N_4O_2$, and melting at 86·5°. On boiling its alkaline solution, it is decomposed into carbonic acid, ethylamine, and diazobenzimide, according to the equation:—

$$C_9H_{12}N_4O_2 = C_6H_5.N_3 + C_2H_5.NH_2 + CO_2.$$

From this reaction, and from the known constitution of the nitroso-body, $C_6H_5—N<{NH_2 \atop NO}$, which is formed from nitrous acid and phenylhydrazine, the constitution of these bodies is inferred to be the following:—



$$\begin{array}{l} C_6H_5—N—NH.CO.NH.C_2H_5 \\ \qquad\;\;\; | \\ \qquad\;\; NO \end{array}$$

Ethylphenylnitroso-semicarbazide.

$$C_6H_5.NH.NH.CO.NH.C_2H_5.$$

Ethylphenyl-semicarbazide.

Numerous attempts to obtain, by reduction of the above nitroso-compound, a base containing three N-atoms similarly combined, led in all cases to negative results.

Phenylsemicarbazide, $C_6H_5—NH.NH.CO.NH_2$, obtained by the action of potassium cyanate upon the neutral salts of phenylhydrazine, crystallises in colourless plates, which melt at 170°. It exhibits in all its relations perfect analogy to the preceding compound.

Phenylhydrazine and Carbon disulphide unite at ordinary temperatures, with considerable evolution of heat, to form phenylhydrazine phenylthiocarbazate, $(C_6H_5.N_2H_3)_2CS_2$. This compound crystallises from its ethereal solution in six-sided prisms which melt at 76—77°.

From a consideration of the general constitution of the thiocarbamates, the author assigns to this body the constitution—

$$C_6H_5.NH.NH.CS.S.H_4N_2.C_6H_5:$$

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* In support of this, the author cites Neubauer's research on creatinine (*Annalen*, cxxxvii, 288), and the results previously obtained by himself with the rosaniline bases (*Ber.*, ix, 891).

a view which derives considerable support from the fact that by the action of acids the body is resolved into phenylhydrazine and free phenylthiocarbazic acid, $C_6H_5.NH.NH.CS.SH$. This acid has been obtained crystallising in shining plates. It is an unstable compound; in ethereal solution it is decomposed after a short time into the salt just described, with simultaneous formation of CS_2.

Diphenylthiocarbazide, $(C_6H_5.N_2H_2)_2CS$, is the chief product of the decomposition of the two preceding compounds by heat (90°). It crystallises in colourless, three-sided prisms. By the action of heat (150°) upon the dry substance, or, better, by treatment of the same with dilute alkalis, it is converted into a compound which is soluble in chloroform, and is precipitated from this solution, on addition of alcohol, in microscopic needles of a blue-black colour. This body is a colouring-matter of some beauty. Its solution in chloroform is beautifully dichroic, the dark-red of the thicker strata passing, on dilution, into a bright green of great intensity. The same solution when treated with bromine yields substitution-products, characterised by the brilliant metallic reflection of the solid substance.

The alkaline solution of this body is rapidly reduced by zinc dust; and on filtering and exposing the colourless solution thus obtained to the air, a fine violet-red colour is developed; and on acidifying the solution, a new colouring-matter is precipitated in the form of red crystalline flocks.

The analysis of the original compound appears to indicate a difference in composition from diphenylthiocarbazide of 2 at. H; it is, however, probably an isomeride. It is to some extent analogous to Liebermann's phenol colouring-matters, but differs from them in containing sulphur, which appears to play the part of oxygen in the chromogenic group.

Diphenylthiosemicarbazide, $C_6H_5.N_2H_2.CS.NH.C_6H_5$, is prepared by mixing alcoholic solutions of the phenyl base and isothiocyanic ether: it crystallises in colourless prisms, which melt at 177°. This body is easily soluble in the dilute alkalis, forming a colourless solution, from which it is precipitated unchanged on the addition of an acid. This proves that both the hydrazine groups of diphenylsulphocarbazide concur to produce the colouring-matter previously described.

Phenylhydrazin Phenylcarbaziate, $(C_6H_5.N_2H_2)_2CO_2$, is obtained as a white crystalline mass by the action of carbonic acid upon the base in presence of water.

Amido-derivatives.—Two of the H-atoms of phenylhydrazine may be successively replaced by acid radicles; of these the first to be replaced is invariably an atom of the NH_2-group: which of the remaining atoms is replaced by the second group has not been ascertained.

Monobenzoylphenylhydrazine, $C_6H_5.N_2H_2.CO.C_6H_5$, prepared by the action of benzoyl chloride upon phenylhydrazine in presence of ether, crystallises in slender white prisms, which melt at 168°. If the solution of this body in chloroform be treated with yellow oxide of mercury, and the solvent evaporated, a dark red-coloured oil remains, which the author concludes to be benzoyldiazobenzene, $C_6H_5.N = N.CO.C_6H_5$.

His attempts to prepare this body synthetically from diazobenzene-compounds and benzaldehyde were unsuccessful.

Dibenzoylphenylhydrazine, $C_6H_5.N_2H.(CO.C_6H_5)_2$, is best prepared by the action of benzoyl chloride upon potassium phenylhydrazinesulphonate, according to the equation :—

$$C_6H_5.N_2H_2.SO_3K + H_2O + 2C_6H_5.COCl = C_6H_5.N_2H.(CO.C_6H_5)_2 + KHSO_4 + 2HCl.$$

The yield of this product approaches the theoretical. It crystallises in slender white prisms, which melt at 177—178°. Heated with concentrated hydrochloric acid at 100° it is resolved into benzoic acid and hydrazine.

Monacetylphenylhydrazine, $C_6H_5.N_2H_2.CO.CH_3$, crystallises in six-sided prisms, which melt at 128·5°, and may be distilled at a higher temperature for the most part unchanged. By the action of mercuric oxide on the solution of this body in chloroform, it undergoes a decomposition precisely similar to that of the benzoyl compound previously mentioned, *acetyldiazobenzene*, $C_6H_5.N{=}N.CO.CH_3$, being formed.

Oxalyldiphenylhydrazine, $(C_6H_5.N_2H_2)_2[CO]_2$, is exactly analogous, both in its constitution and mode of formation, to oxamide. It is a crystalline body, melting at 277—278°; at a somewhat higher temperature it distils practically unchanged.

Phenylbenzene-thiazide, $C_6H_5.NH.NH.SO_2.C_6H_5$, is prepared by the action of benzene-thiochloride upon phenylhydrazine in ethereal solution. It crystallises in thin white needles which melt at 146°. By oxidation with mercuric oxide it is converted into the diazo-compound, $C_6H_5.N{=}N.SO_2.C_6H_5$, described by Königs (*Ber.*, x, 1531), who obtained it by the action of benzenesulphinic acid upon diazobenzene.

Trinitrohydrazobenzene, $C_6H_5.NH.NH.C_6H_2.(NO_2)_3$, is analogous in constitution and mode of preparation to picramide. It crystallises in red shining plates which melt at 181°. By reducing agents it is resolved into aniline and an aromatic base, which has not been further investigated. By the action of mercuric oxide on its alcoholic solution it is converted into trinitroazobenzene, $C_6H_5.N{=}N.C_6H_2.(NO_2)_3$. This body crystallises from its solution in hot alcohol in long, slender, red prisms, which melt at 142°.

Similar compounds were obtained from phenylhydrazine and dinitrochlorobenzene. The reaction seems in effect to afford a convenient general method for the preparation of the substitution-products of azo- and hydrazobenzene.

Phenylhydrazine and the aldehydes unite, with elimination of water, to form in nearly all cases well crystallised, indifferent bodies, containing the residues of 1 mol. of each reagent: in this respect they differ from the otherwise similar derivatives of the ordinary amine bases. The following are described :—

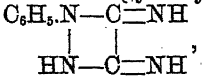
Benzylidene-phenylhydrazine, $C_6H_5.N_2H.CH.C_6H_5$, crystallises in well defined prisms, which melt at 152·5°. At a higher temperature this body distils unchanged.

Ethylidenephenylhydrazine, $C_6H_5.N_2H.CH.CH_3$, occurs in colourless crystals.

Phenylfurfurazide, $C_6H_5.N_2H.C_5H_4O$, crystallises in plates of a pale-yellow colour, which melt at 96°, and decompose at higher temperatures. By reason of the simplicity of the constitution of this, as compared with the compounds of furfurol with other amines, it will doubtless form a valuable aid in the solution of the constitution of furfuramide and furfurine.

Phenylhydrazine and cyanogen gas unite, in presence of water, to form a crystalline compound which, after purification, is obtained in the form of plates which are nearly free from colour. This body melts at about 160° with partial decomposition, and is wholly decomposed at higher temperatures.

Its constitution appears to be that of phenyldicyanhydrazine, $C_6H_5.N_2H_3.(CN)_2$, or, from its analogy to cyananiline, to be that represented by the formula



$$\begin{array}{l} C_6H_5.N—C{=}NH \\ \quad\quad\;\; | \quad\;\; | \\ \quad\;\; HN—C{=}NH \end{array}$$

, though at the same time the assumption of a closed chain of N- and C-atoms is somewhat improbable. Its solution in the aqueous alkalis is characterised by a rapid absorption of oxygen from the air, accompanied by the development of a dark-brown colour. It undergoes but a very partial decomposition on heating with hydrochloric acid to 100°. Heated for some hours with water at 150°, it is converted into a body which crystallises in thin white needles, but has not been further investigated. With nitrous acid it yields a white crystalline body which is probably a nitroso-derivative.

Action of Sulphur upon Phenylhydrazine.—Amongst the products of heating these bodies together to 130°, the following compounds were identified:—

$$N;\ NH_3;\ H_2S;\ C_6H_6;\ C_6H_5.HS;\ (C_6H_5)_2S;\ (C_6H_5)_2S_2 \text{ and } C_6H_5.NH_2.$$

The action of sulphur upon the hydrazines is, therefore, for the most part limited to their nitrogenous group, and is similar to the decomposition of these bases by oxidation in their alkaline solution. The formation of aniline, which occurs to the extent of 30 per cent. of the phenylhydrazine employed, is explained by the equation:—

$$2(C_6H_5.NHNH_2) + S = 2(C_6H_5.NH_2) + H_2S + N_2;$$

that of benzene and the various sulphur-derivatives enumerated resembles the ordinary decomposition of the diazo-compounds.

Methylphenylhydrazine, when subjected to the action of nitrous acid under regulated conditions, undergoes a remarkable decomposition into methylphenylnitrosamine and nitrous oxide; thus:—

$$\left.\begin{matrix} C_6H_5 \\ CH_3 \end{matrix}\right\} N_2H_2 + 2HNO_2 = \left.\begin{matrix} C_6H_5 \\ CH_3 \end{matrix}\right\} N_2O + N_2O + 2H_2O.$$

Since there is no warrant for assuming the direct oxidation of an NH_2- to an NO-group, and since, therefore, this reaction is the inverse of that by which the original base was formed, the author represents the decomposition as occurring in two stages; the first consisting in the resolution of the base into methylaniline and hydroxylamine, thus :—

$$\left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\}N\text{—}NH_2 + H_2O = \left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\}NH + H_3NO,$$

and these bodies being in the second place at once resolved by nitrous acid into methylphenylnitrosamine and nitrous oxide respectively.

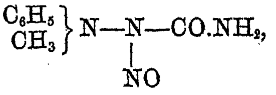
Methylphenylhydrazine and Diazobenzene, when brought together in cold aqueous solution, the latter being in the form of nitrate, were found to enter into energetic reaction, the chief products of which were diazobenzimide and methylaniline. The reaction may be formulated as follows :—

$$\left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\}N\text{—}NH_2 + C_6H_5.N_2.NO_3 = \left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\}NH + C_6H_5.N_3 + HNO_3.$$

A third body was also isolated, crystallising in colourless plates, and identical with the product of oxidation of the base by mercuric oxide, to be shortly described. Its formation is probably referable to the action of the nitric acid.

Derivatives of Methylphenylhydrazine.—The formation by this base of well-defined compounds with benzoyl chloride, acetic anhydride, and isocyanic ether, was established by qualitative experiments. The following carbamide-derivatives are described :—

Methylphenylsemicarbazide, $\left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\}N\text{—}NH.CO.NH_2$, is formed by adding potassium cyanate to the solution of the base in hydrochloric acid. It occurs in masses of fine white crystals which melt at 133°. Heated with hydrochloric acid at 100° in sealed tubes, it is decomposed into ammonia, carbonic acid, and phenylhydrazine. By the action of nitrous acid it is converted into the nitroso-derivative,



$$\left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\}N\text{—}\underset{\displaystyle NO}{\underset{|}{N}}\text{—}CO.NH_2,$$

which crystallises in fine bright-yellow plates, melting at 77°.

Methyldiphenylthiosemicarbazide, $\left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\}N.NH.CS.NH.C_6H_5$, is prepared by mixing methylphenylhydrazine and phenylisothiocyanic ether in the proportion of equal numbers of molecules.

It is a crystalline body melting at 154°.

Phenylhydrazine and the halogens unite with considerable energy; the reaction is most easily controlled and investigated in the case of iodine. By the alternate addition of iodine and caustic potash to water holding the base in suspension, the latter is wholly decomposed into diazobenzimide, aniline, and small quantities of substituted anilines; probably according to the equation :—

$$2C_6H_5.N_2H_3 + 2I_2 = C_6H_5.N_3 + C_6H_5.NH_2 + 4HI.$$

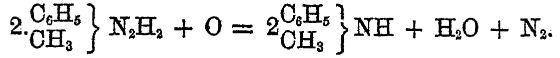
The analogy of this to the decomposition of the base by oxidation in its acid solution is evident.

Secondary Aromatic Hydrazines.—These bodies are isomeric with the hydrazo-compounds, from which they differ in being constituted after the unsymmetrical type $R_2{=}N{-}NH_2$. They are easily obtained by the reducing action of zinc-dust and acetic acid upon the nitroso-derivatives of the secondary amines, of which they are, in fact, the sole products.

Methylphenylhydrazine, $C_6H_5.N_2H_2.CH_3$, is a colourless oil which remains liquid at $-17°$; it boils at 222—224°, at a temperature, therefore, 10° lower than phenylhydrazine.* This base, in common with all similar secondary hydrazines, is more stable in contact with oxidising agents than the primary bases: it reduces Fehling's solution only when heated. It is a monacid base: its sulphate has the composition $\{C_6H_5.N_2H_2.CH_3\}_2H_2SO_4$: it crystallises in white shining plates which are easily soluble in water. The constitution of this body is established beyond doubt by its synthesis from methylphenylnitrosamine, $\left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\}N{-}NO$, to be that represented by the formula $\left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\}N{-}NH_2$; and this view derives much support from the fact that all the reactions of phenylhydrazine, in which the NH_2-group comes into play, are equally characteristic of this base, whereas no reaction of the former body, which may be regarded as determined by its NH-constituent, has been observed to occur in the case of methylphenylhydrazine.

As a tertiary base, it unites directly with 1 mol. C_2H_5Br and C_2H_5I to form well crystallised bodies which exhibit all the reactions of ammonium compounds.

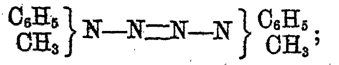
Oxidation of Methylphenylhydrazine.—The aqueous solution of the base, when heated with Fehling's solution, is decomposed according to the equation :—



$$2.\left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\}N_2H_2 + O = 2\left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\}NH + H_2O + N_2.$$

By the action of mercuric oxide on the solution of the base in chloroform the crystalline compound is obtained, which was mentioned as occurring amongst the products of decomposition of the base by diazobenzene nitrate. It melts at 133°; its empirical composition is represented by the formula $C_7H_8N_2$. It is decomposed with explosive violence when strongly heated; its reactions are those of an indifferent body.

From the consideration and discussion of its properties and reactions, the author regards this body as probably constituted similarly to the azo-bodies, and represented, therefore, by the formula—



$$\left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\}N{-}N{=}N{-}N\left\{\begin{matrix}C_6H_5\\CH_3\end{matrix}\right.;$$

its formation, therefore, is entirely analogous to that of azobenzene from aniline. On this view it would be designated "Dimethyl-diphenyl-tetrazone." This body yields with iodine an addition-product which crystallises in thin black needles; they are, however, very unstable. Their composition appears to be represented by the formula $C_{14}H_{16}N_4I_4$.

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* A depression of the boiling point of liquids consequent upon the replacement of H by an alcohol-radicle, has been observed by Michler (*Ber.*, viii, 1865) to occur also in the substituted carbamides.

Diphenylhydrazine, $(C_6H_5)_2N_2H_2$, is formed from the corresponding nitrosamine by reduction with zinc and acetic acid. It is a yellowish oil, which does not solidify at −17°. Its hydrochloride crystallises in slender colourless needles. The concentrated aqueous solution is dissociated on gently heating, but recombination occurs at higher temperatures. The sulphate, $\{(C_6H_5)_2.N_2H_2\}_2H_2SO_4$, and nitrate also crystallise in slender needles.

Monobenzoyldiphenylhydrazine, $(C_6H_5)_2N_2H.COC_6H_5$, is obtained by the action of benzoyl chloride upon the base in presence of ether. It crystallises in slender white shining needles which melt at 192°.

Benzylidene-diphenylhydrazine, $(C_6H_5)_2.N_2.CH.C_6H_5$, results from the union of diphenylhydrazine and benzaldehyde with elimination of water. It is a crystalline body, melting at 122°, 30° lower, therefore, than benzylidine*mono*phenylhydrazine. From the synthesis of this body the author deduces the constitutional formula $(C_6H_5.)_2N—NH_2$.

The relations of this body to its isomeride, hydrazobenzene, $C_6H_5—NH—NH—C_6H_5$, which are indicated by the above formulæ, are entirely in harmony with the results of experiment. Of these we may mention the following:—

Diphenylhydrazine forms stable salts with the mineral acids; in no case are these reagents observed to bring about the molecular rearrangement by which its isomeride is converted into benzidine. Subjected to dry distillation, the former is partially decomposed into ammonia and diphenylamine; the latter completely into aniline and azobenzene.

The most trustworthy index of the nature of this isomerism lies in the behaviour of these bodies towards nitrous acid. This reagent converts hydrazobenzene, under regulated conditions, into a body which closely resembles the ordinary nitrosamines; diphenylhydrazine is decomposed into diphenylnitrosamine and nitrous oxide, according to the equation:—

$$(C_6H_5)_2N_2H_2 + 2HNO_2 = (C_6H_5)_2N_2O + N_2O + 2H_2O.$$

The probable intermediate stages of this resolution have been discussed in treating of the similar decomposition of methylphenylhydrazine.

Oxidation of Diphenylhydrazine.—This base is readily oxidised by mercuric oxide. In warm solutions the action takes place according to the equation:—

$$2[(C_6H_5)_2N.NH_2] + O = 2(C_6H_5)_2NH + H_2O + N_2.$$

In cold dilute solutions, a crystalline body melting at 123° is obtained, apparently *tetraphenyltetrazone*, $(C_6H_5)_2{=}N—N{=}N—N{=}(C_6H_5)_2$.

C. F. C.

Methyl-violet and Diphenylamine-blue. By H. Brunner and R. Brandenburg (*Deut. Chem. Ges. Ber.*, x, 1844—1848).

Methyl-violet.—According to the opinion of Gräbe and Caro (*Liebig's*

Annalen, clxxix, 189), tetramethyl-rosaniline is the basis of methyl-violet; in accordance with this opinion the authors allowed 3 mols. of bromine to react on 3 mols. of dimethylaniline, according to the equation, $3C_6H_5N(CH_3)_2 + 3Br_2 = 6HBr + C_{20}H_{15}(CH_3)_4N_3$, and obtained a resinous mass from which by purification they obtained a body colouring silk a blue violet, and having the formula $C_{20}H_{15}(CH_3)_4N_3 + 4HBr$. When heated above 120°, this body loses hydrobromic acid, and gives a series of compounds which impart to silk a reddish-violet colour, the violet becoming more red with increasing loss of *hydrobromic acid.*

Diphenylamine-blue.—This compound has been obtained by the action of 3 mols. of bromine on a solution of 2 mols. of diphenylamine and 2 mols. of toluidine in glacial acetic acid, as follows:—

$$2C_{12}H_{11}N + 2C_7H_9N + 3Br_2 = NH_3 + 6HBr + \underset{\text{Triphenyl-rosaniline.}}{C_{20}H_{16}(C_6H_5)_3N_3}.$$

By the purification of the mass obtained by heating the whole at 150° for some time, then to 180°, a blue-colouring base was obtained, which with sulphuric acid yields a sulpho-compound soluble in water and colouring wool blue.

By the action of bromine on aniline and solid or liquid toluidine, fuchsine and a blue-violet dye-stuff were obtained. P. P. B.

Sulphonic Acids of Normal Butylbenzene. By L. BALBIANO (*Gazzetta chimica italiana*, vii, 343—347).—The normal butylbenzene was prepared, according to Fittig's general method, by treating bromobenzene and butyl bromide dissolved in benzene with sodium, and heating gently. Pure butylbenzene obtained from the product by fractional distillation is a colourless liquid, of aromatic odour, boiling at 179·5°—180·5° under a pressure of 748 mm., corresponding exactly with the compound obtained by Radziszewski. Its density is 0·875 at 0°, and 0·864 at 15°. When treated with a mixture of Nordhausen and ordinary sulphuric acids it yields two sulphonic acids, which may be separated by the difference in solubility of their barium salts. That which occurs in largest quantity is anhydrous and less soluble than the other. It forms small unctuous plates of the formula $C_{20}H_{26}S_2O_6Ba$. The lead salt, $C_{20}H_{26}S_2O_6Pb.H_2O$, crystallises in stellate groups of needles. The free acid obtained by decomposition of the lead salt with sulphuretted hydrogen, forms when evaporated in a vacuum a hygroscopic crystalline mass which is very soluble. The calcium salt resembles the barium salt, whilst the zinc salt, $C_{20}H_{26}S_2O_6Zn.7H_2O$, forms very soluble needles.

The hydrated baric salt of the second sulphonic acid crystallises in nodules of the formula $C_{20}H_{26}S_2O_6Ba.2H_2O$, which are moderately soluble in cold water. The lead salt, $C_{20}H_{26}S_2O_6Pb.2H_2O$, forms microscopic plates. The free acid corresponding to these salts is very hygroscopic, and may be prepared from the lead salt in the usual way. The author, with a view of confirming the existence of these two sulphonic acids derived from normal butyl-benzene, intends to prepare the corresponding ethers, and compare their properties. C. E. G.

Preparation of Quinones and Hydroquinones. By R. NIETZKI (*Deut. Chem. Ges. Ber.*, x, 1934—1935).—The process described by the author is based upon the fact, observed by himself, that quinone and hydroquinone are produced in the oxidation of aniline-black by chromic acid.

Hydroquinone is prepared as follows:—One part of aniline is dissolved in 8 parts of sulphuric acid diluted with twice its bulk of water: to this solution, after cooling, a saturated solution of $2\frac{1}{2}$ parts of potassium bichromate is added gradually, too great a rise of temperature being avoided. The thick pulpy mass of aniline-black produced at first changes after a time to a dirty-brown solution, which is then to be treated with sulphur dioxide in excess, and afterwards agitated with ether. The ethereal liquid, when distilled, leaves a brownish crystalline residue of crude hydroquinone, amounting to 16 per cent. of the aniline employed.

Hydrotoluquinone may be prepared in the same manner from orthotoluidine.

For the preparation of quinones, the proportion of the oxidising agent must be increased; and it is found best to add the latter in small quantities, and after each addition to distil off the quinone produced. Toluquinone is formed with facility: it may be readily distinguished from quinone, not only by its much lower melting-point, but also by its crystalline form, toluquinone forming pointed rhombic laminæ, whereas quinone forms long, very thin needles.

Hydroquinone and hydrotoluquinone dissolve readily in hot crude toluene, and crystallise therefrom almost entirely on cooling.

J. R.

Some Colouring-matters derived from Phenol, Rosolic Acid, Aurin, Corallin, and Azurin. By C. ERHART (*Arch. Pharm.* [3], viii, 481—510).—This investigation was commenced before Dale and Schorlemmer, and Fresenius and Kolbe published their results; it has for its object a comparison of the above-named bodies with each other and with other colouring-matters derived from phenol.

Runge's experiment of distilling phenol with milk of lime was repeated. From 1 kilogram, only 2 or 3 grams of an impure substance exhibiting green reflections were obtained, and its purification was not undertaken. Müller's process of exposing phenate of calcium to air for some months was carried out. The phenol was removed from the dark-red product by boiling with water, the impurities filtered off, and, on addition of hydrochloric acid, orange flocks were precipitated. This substance was purified by repeated solution in ammonia and precipitation with carbonic acid. Thus prepared, the colouring-matter is indistinctly crystalline, and melts at 159—160°.

It dissolved in all the usual solvents, benzene excepted. In alkalis, it dissolved with a purple-red colour; the other solutions were brown. Ammonia had no decided action on this substance, either when in the form of aqueous ammonia or in the gaseous state; on addition of alcohol, however, a compound separated, which lost every trace of ammonia when heated to 120°. This substance differs from corallin in not giving a blue, but a brownish-black colouring-matter when heated with aniline. The compounds of rosolic acid, thus prepared, with the alkaline earths, lead, &c., are very indefinite and give no indication of the molecular weight. Its formula before drying is $C_{18}H_{16}O_5$, and after being heated to 159°, $C_{18}H_{14}O_4$. It appears therefore to lose 1 molecule of water when heated. The hypothetical equation given by the author to represent the formation of this substance, supposes 2 atoms of hydrogen in the C_6H_5 group of phenol to be replaced by calcium.

After alluding to the results obtained by Wichelhaus in oxidising phenol, the author notices that phenoquinone, $C_6H_4(O.OC_6H_5)_2$ is isomeric with rosolic acid, but from their reactions these two bodies clearly differ in constitution. He then describes the preparation of rosolic acid from rosaniline by nitrous acid, or by water under pressure. From this reaction it appears probable that as rosaniline is derived from a mixture of aniline and toluidine, so rosolic acid is a derivative of phenol and kresol, or from phenol and some substance capable of adding an atom of carbon. Phthaleïn stands in close relation to these compounds.

Dale and Schorlemmer's formula for aurin extracted from a commercial sample, is $C_{24}H_{18}O_8$, omitting the water, which formula they subsequently altered to $C_{20}H_{14}O_3 + H_2O$ (at 110°).—See this Journal, 1872, p. 75, and 1877, ii, 121.—Fresenius' formula is $C_{40}H_{38}O_{11} = 2C_{20}H_{14}O_3 + 2\frac{1}{2}H_2O$. The chief difference between the two is, that Dale and Schorlemmer's aurin may be heated to over 200° without decomposition, whereas Fresenius' sample decomposes at 170°.

The author's own experiments give the following results:—Commercial aurin contains 5 or 6 per cent. of sulphur, which is very difficult to remove, and cannot be reduced below 0·25 per cent. Some rosolic acid was made by the author from phenol sulphuric acid and oxalic acid, and purified by washing, subsequent solution in alkali and precipitation with carbonic acid, and finally by crystallisation from alcohol or from glacial acetic acid. Thus prepared, it melted at 154—155°. From numerous analyses it was found to have the formula $C_{40}H_{38}O_{11}$. Both in its formula and behaviour on heating, it coincided with Fresenius' aurin, and differed from that of Dale and Schorlemmer. By analysing the gas given off during the action of the sulphuric and oxalic acids on phenol, the author draws conclusions similar to those of Kolbe and Fresenius, viz., that the formation of aurin is due to nascent carbon monoxide. From the manner in which the product lost water on drying, it appears to contain $3H_2O$ as water of crystallisation, and $2H_2O$ in more intimate combination; after the last portions of water have been expelled, corallin no longer gives a clean azuline reaction.

Azulin or azurin, first prepared by the manufacturers, Guinon, Marnas, and Co., at Lyons, was obtained by boiling moderately-pure corallin with 8—40 times its weight of aniline. Corallin dissolves in chloroform, amyl alcohol, acetic, oxalic, and tartaric acids. In sulphuric acid, it dissolves with a hyacinth-red colour, and is precipitated on addition of water. The azulin was prepared for analysis by exhaustion with cold ether and solution in hot acetic acid; the portion which separated on cooling was repeatedly boiled with dilute acid and alkali, and the residue washed and dissolved in alcohol. From this solution the colouring-matter separated in hard crusts, very indistinctly crystalline. It had the colour of sublimed indigo, and melted at 146°. It contained no water. Its formula was found to be $C_{26}H_{22}N_2O_2$, and its formation may be expressed by the equation—

$$C_{20}H_{16}O_4 + 2C_6H_7N = C_{26}H_{22}O_2N_2 + C_6H_5OH + H_2O.$$

The author suggests the following constitutional formulæ for aurin and azulin:—

$$\underset{\text{Aurin.}}{C_6H_3(OH)\equiv(CO)_2\equiv(C_6H_5)_2.} \qquad \underset{\text{Azulin.}}{(C_6H_5)_2N_2H_2\equiv(CO)_2\equiv(C_6H_5)_2.}$$

or, if the formula of the latter be halved, it would be, $CO<\begin{matrix}C_6H_5\\C_6H_5NH\end{matrix}$.

Since the communication of which the above is an abstract was written, the results of other researches on this subject have been published. Commercial rosolic acid has been found by Zulkowsky to consist of a mixture of two substances, one identical with Dale and Schorlemmer's aurin, and the other amorphous. Aurin has been synthetically prepared by Liebermann and Schwarzer from phenol and salicylic aldehyde. thus:—$C_6H_6O + 2C_7H_6O_2 = C_{20}H_{14}O_3 + 2H_2O$. And lastly, Zulkowski suggested that rosaniline and rosolic acids are respectively the triamide and trihydroxyl derivatives of a hydrocarbon, $C_{20}H_{18}$, which has since been obtained by O. and E. Fischer.

W. R.

Synthesis of Benzoic Acid and Benzophenone by the aid of Carbonyl Chloride. By A. FRIEDEL, L. CRAFTS, and E. ADOR (*Deut. Chem. Ges. Ber.*, x, 1854—1858).—The authors have failed to obtain any result from the action of chlorcarbonic ether on benzene in presence of aluminic chloride. When, however, carbonyl chloride, which is absorbed in the cold by benzene, is used, it acts on benzene in presence of aluminic chloride in such a manner that when the action takes place slowly benzophenone is produced, and a very little benzoic acid. If the reaction is allowed to take place rapidly, benzoyl chloride and benzoic acid are formed. Thus the reaction appears to take place as follows:—

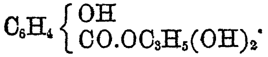
$$(1.)\ C_6H_6 + COCl_2 = C_6H_5COCl + HCl.$$
$$(2.)\ C_6H_6 + C_6H_5COCl = C_6H_5COC_6H_5 + HCl.$$

P. P. B.

Formation of Ferrous Salicylate. By S. BARILALI (*Gazzetta chimica italiana*, vii, 358—360).—This paper contains the results obtained by the author when endeavouring to prepare ferrous salicylate. The coloured solution produced when salicylic acid is added to an iron salt, after evaporation at 100°, does not entirely redissolve, but leaves a residue of ferric oxide. Salicylic acid dissolves metallic iron with disengagement of hydrogen, forming a pale rose-coloured solution, which rapidly becomes darker on exposure to the air; the iron at the same time becomes covered with a greenish crust, which the author considers to be a basic salicylate of iron. This green colour changes to deep red on exposure to the air.

C. E. G.

A New Ether of Glycerin. By CHRISTIAN GÖTTIG (*Deut. Chem. Ges. Ber.*, x, 1817—1819).—The salicylic ether of glycerin is prepared by dissolving salicylic acid in glycerin and passing hydrochloric acid gas through this solution heated to 100°. The ether so obtained is purified, after washing, by distilling under reduced pressure, as it decomposes when distilled under the ordinary pressure. It is a colourless and odourless liquid, soluble in alcohol, ether, and carbon disulphide. Analysis shows it to have the formula—



$$C_6H_4\left\{\begin{matrix}OH\\ CO.OC_3H_5(OH)_2\end{matrix}\right..$$

The author supposes that the hydrochloric acid acts so as to form first the monochlorhydrin of glycerin, and not salicyl chloride.

P. P. B.

Parabromometasulphophenylpropionic and Metasulphophenylpropionic Acids. By T. GÖRING (*Chem. Centr.*, 1877, 793—800, and 808—815).—By the action of bromine on phenylpropionic acid different products are formed, about one-third consisting of parabromophenylpropionic acid, which is less soluble in carbon sulphide than the other bodies, and separates from a hot solution as a mealy powder, but on slow evaporation is obtained in flat glistening needles, melting at 135°.

By the action of fuming sulphuric acid, it is converted into a monosulphonic acid, crystallising in non-deliquescent rhombic plates or prisms, containing $C_9H_9BrSO_5 + 2\frac{1}{2}H_2O$; $a : b : c = 1{\cdot}3013 : 1 : 0{\cdot}7831$.

$C_9H_7BrSO_5Ba + 2H_2O$ forms crystalline crusts, and $(C_9H_8BrSO_5)_2Ba + 8H_2O$ well-defined monoclinic crystals; $a : b : c = 0{\cdot}4941 : 1 : 0{\cdot}5065$.

$C_9H_7BrSO_5Ca + 3H_2O$ is a crystalline powder, and $(C_9H_8BrSO_5)_2Ca + 8H_2O$ forms monoclinic crystals; $a : b : c = 0{\cdot}7062 : 1 : 0{\cdot}9774$.

The *normal sodium salt* crystallises in deliquescent needles, and the acid salt forms prisms with 3 molecules of water. The *normal potassium salt* is very soluble, and does not crystallise well, and the less soluble acid salt forms needles. The *normal copper* and *silver salts* separate on evaporation in crusts, consisting of microscopic needles. The *zinc salt* is a gummy mass, in which, on standing in the air, crystalline salts appear. The *lead salt* forms glistening crystals.

On treating the acid with sodium amalgam, the bromine is replaced by hydrogen, and the *sulphophenylpropionic acid* thus obtained yields, on melting with potash, pure metoxybenzoic acid.

In the preparation of the *bromosulphonic acid*, two other bodies are formed; one is insoluble in water, and present in very small quantity only; the other is volatile with steam, forms thin rhombic plates melting at 112°, smells like benzaldehyde, reduces an ammoniacal silver solution, and on analysis gives numbers agreeing with those required for a bromocinnamaldehyde.

C. S.

Oxybenzoic Acids. By HUGO KUPFERBERG (*J. pr. Chem.*, xvi, 424—447).—Sodium paraoxybenzoate, when heated to 240—250°, is resolved into the basic salt, phenol, and carbonic anhydride, as follows:—

$$2C_6H_4(OH)CO_2Na = C_6H_4(ONa)CO_2Na + C_6H_5OH + CO_2.$$

The basic salt is left as a white residue if the operation is conducted in a stream of CO_2 and the temperature raised to 280—295°. The residue is then found to yield 36 per cent. of salicylic acid, the quantity decreasing with the rise of temperature. The change of paraoxybenzoic acid into salicylic acid the author views as due to the action of carbonic acid, and to a more complex action than the change of position of the hydroxyl and carbonyl groups. Perhaps it is owing to the formation of an isomeride of orthophenoldicarbonic acid, which on heating would be resolved into basic sodic salicylate and carbonic anhydride, as follows:—

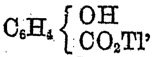
$$C_6H_3(OH)(CO_2Na)_2 = C_6H_4(ONa)CO_2Na + CO_2.$$

This theory is supported by the following observations:—(1.) When sodic paraoxybenzoate is heated in a quick stream of hydrogen, no salicylic acid is formed; if the stream is slow, a small quantity is formed. (2.) Van den Welden's observation (*J. pr. Chem.* [2], xv, 155), that thallious salicylate when heated decomposes into paraoxybenzoic and orthophenoldicarbonic acids. (3.) Ost's observation (*J. pr. Chem.* [2], xv, 306), that basic potassic paraoxybenzoate is resolved into potassic orthophenoldicarbonate when heated. (4.) A nearer examination of the product obtained by heating sodic paraoxybenzoate in a stream of CO_2 showed the presence of orthophenoldicarbonic, $C_6H_3(OH)(CO_2H)_2$, and oxytrimesitic acid, $C_6H_2(OH)(CO_2H)_3$. By conducting the operation very slowly, the end-product was found to contain basic sodic oxytrimesitate only, the reaction taking place as follows:—

$$2C_6H_4(ONa)CO_2Na + CO_2 = C_6H_2(ONa)(CO_2Na)_3 + C_6H_5.OH.$$

Potassic paraoxybenzoate heated to 240—250° in a stream of CO_2 is resolved into basic potassic paraoxybenzoate, phenol, and CO_2; small quantities of orthophenoldicarbonic and oxytrimesitic acids are formed, due to the fact that the potassium salt of the former acid is decomposed at high temperatures into basic paraoxybenzoate and CO_2.

The identity of the orthophenoldicarbonic and oxytrimesitic acids obtained above with those obtained from salicylic acid is fully borne out by their characters. The alkaline salts of oxybenzoic acid differ from those of the isomeric acids in their behaviour on heating; they yield no basic salts, and only a small amount of impure phenol, the residue becoming carbonised.



Thallious oxybenzoate, $C_6H_4\left\{\begin{matrix}OH\\CO_2Tl\end{matrix}\right.$, prepared by neutralising the acid with thallious carbonate and evaporating the solution, crystallises in colourless shining prisms, easily soluble in hot, less so in cold water. Basic thallious oxybenzoate, prepared by heating aqueous solution of oxybenzoic acid with excess of thallious hydrate, and evaporating the solution, crystallises in yellow prisms more soluble than the neutral salt, and possesses an alkaline reaction.

The basic alkaline oxybenzoates are white hygroscopic powders, which on heating in a stream of CO_2 leave a residue containing only oxybenzoic acid.

Tetrethylammonium Salicylate, $C_6H_4\left\{\begin{matrix}OH\\CO_2(C_2H_5)_4N\end{matrix}\right.$, prepared by neutralising the aqueous solution of the base with salicylic acid, and evaporating the solution, is a brown, syrupy, highly hygroscopic mass. On heating to 150°, it is resolved into triethylamine and ethyl salicylate. The oxybenzoate of this base resembles the salicylate, the paraoxybenzoate is, however, resolved at 170° into CO_2, triethylamine, ethylparaoxybenzoate, and phenetol, as follows:—

$$C_6H_4\left\{\begin{matrix}OH\\CO_2(C_2H_5)_4N\end{matrix}\right. = C_6H_5OC_2H_5 + (C_2H_5)_3N + CO_2.$$

Triethylphenylammonium Oxybenzoates, $C_6H_4\left\{\begin{matrix}OH\ \ C_6H_5\\CO_2(C_2H_5)_3\end{matrix}\right\}N$, are more stable than those of tetrethylammonium, but are decomposed by heat in a similar manner, yielding diethylphenylamine and the ethyl-ether of the acid.

Methylamine Salicylate and *Paraoxybenzoate*, $C_6H_4\left\{\begin{matrix}OHCH_3\\CO_2H\end{matrix}\right\}N$, are deliquescent crystalline masses, which are resolved by heat into methylamine, phenol, and CO_2. The oxybenzoate, however, yields on heating, methylamine and oxybenzoic acid.

The *aniline oxybenzoates*, prepared by dissolving equivalent quantities of base and acid in alcohol, and evaporating the solution, are well crystallised compounds, and are decomposed by heat in a similar manner to the methylamine salts, the paraoxybenzoate yielding a small quantity of the anilide.

The three oxybenzoyl-anilides are prepared by heating the aniline salts with PCl_3 or P_2O_5 as crystalline bodies.

Salicyl-anilide crystallises in prisms melting at 132° (Wanstrat 134—131°, *Deut. Chem. Ges. Ber.*, vi, 336).

Paraoxybenzoyl-anilide crystallises in yellow shining plates, melting at 196—197°.

Oxybenzoyl-anilide crystallises in white silky needles, melting at 154—155°.

The anilides are all easily soluble in alcohol, and are difficultly soluble in water; with the alkali metals and thallium they form easily soluble compounds by the replacement of the hydrogen in the hydroxyl group by metal, their solutions yielding amorphous precipitates with salts of the heavy metals. Salicyl-anilide differs from the others in giving a violet coloration with ferric chloride. P. P. B.

Action of Dilute Sulphuric Acid on Hydrobenzoïn and Isohydrobenzoïn. By A. Brewer and Th. Zincke (*Deut. Chem. Ges. Ber.*, xi, 72—78).—The authors have further examined the products of this action, which were described in a previous paper (*Deut. Chem. Ges. Ber.*, ix, 1769; *Journ. Chem. Soc.*, 1877, i, 460).

The liquid products they believe to be diphenylacetic aldehyde, from the fact that they yield diphenylacetic acid, among other products, when heated with alcoholic potash.

Both the solid products yield, by oxidation with chromic and acetic acids, a compound of the formula $C_{28}H_{22}O_3$, which is soluble in alcohol, ether, benzene, and acetic acid, and crystallises in white needles melting at 154—155°. This substance, by prolonged boiling with acetic and chromic acids, is converted into another crystalline compound, which melts at 97—98°. By reduction with phosphorus and hydriodic acid at 200°, it yields dibenzyl and a second product of the formula $C_{15}H_{13}O_2$. The latter crystallises from hot spirit in brilliant laminæ melting at 144—145°, and is converted by oxidation into benzophenone. The subject is being continued. J. R.

Benzoyl-phenol. By O. DOEBNER and W. STOCKMANN (*Deut. Chem. Ges. Ber.*, x, 1969—1972).—The authors have previously shown that this substance is formed, together with phenyl benzoate, by the action of benzotrichloride on a mixture of phenol and zinc oxide. They have since found that when an excess of benzotrichloride is employed, the product is almost exclusively benzoyl-phenol benzoate, formed by the action of the trichloride on the phenyl benzoate first produced—

$$C_6H_5.CO.OC_6H_5 + ZnO + C_6H_5CCl_3$$
$$= C_6H_5CO.OC_6H_4.COC_6H_5 + ZnCl_2 + HCl.$$

Accordingly, benzoyl-phenol is best obtained by first preparing phenyl benzoate (by heating together equal numbers of molecules of phenyl and benzoyl chloride), and then treating this substance with the calculated quantity of benzotrichloride and zinc oxide, or (what comes to the same thing) of benzoyl chloride and zinc chloride. The benzoyl-phenol benzoate thus produced is decomposed by boiling with alcoholic potash, and the liberated benzoyl-phenol is precipitated from the solution by carbon dioxide.

Benzoyl-phenol benzoate is likewise formed on heating together equivalent quantities of benzoyl-phenol and benzoyl chloride. It crystallises from alcohol in brilliant laminæ, and from ether in large tables, which dissolve freely in acetic acid, benzene, and hot alcohol, but only sparingly in water.

Benzoyl-phenol acetate, $C_6H_5CO.OC_6H_4.COCH_3$, obtained by heating benzoyl-phenol with acetic anhydride, crystallises from weak spirit in groups of long, colourless needles, melting at 81°. It dissolves easily in ether, benzene, and acetic acid, sparingly in water, and is readily decomposed by alkalis.

Benzoyl-phenol, when treated with sodium-amalgam in the cold, takes up 2 atoms of hydrogen, and is converted into *benzhydryl-phenol*, $C_6H_5CH(OH).C_6H_4OH$, which crystallises from the alkaline solution in large needles. The product melts at 161°, and dissolves easily in alcohol, ether, and hot water, and less easily in benzene. Acids precipitate it unaltered from its solutions in alkalis.

Benzoyl-phenol is converted by fusion with potash into paraoxybenzoic acid, benzene being eliminated. J. R.

New Chloronaphthalenes. By A. ATTERBERG and O. WIDMAN (*Deut. Chem. Ges. Ber.*, x, 1841—1844).—The treatment of a chloroform solution of γ-dichloronaphthalene with chlorine gas, yields two addition-products, viz., γ-dichloronaphthalene tetrachloride, $C_{10}H_6Cl_2Cl_4$, crystallising in prisms, melting at 85°; and trichloronaphthalene dichloride, $C_{10}H_5Cl_3Cl_2$, crystallising from alcohol in large, shining crystals, which melt at 93°. On boiling with alcoholic potash, these both yield δ-tetrachloronaphthalene, which crystallises in thin white needles, slightly soluble in alcohol, more so in presence of toluene, and melts at 141°.

Tetrachloronaphthalene yields when nitrated a mononitro-compound, $C_{10}H_3Cl_4(NO_2)$, which crystallises in pale yellow rhombic plates, melting at 154—155°. This nitrochloronaphthalene, heated with PCl_5, yields β-pentachloronaphthalene, $C_{10}H_3Cl_5$, which crystallises in concentrically grouped needles, melting at 177°. β-pentachloronaphthalene yields on oxidation a trichlorophthalic acid, $C_6HCl_3(CO_2H)_2$, which, when sublimed, yields a trichlorophthalic anhydride melting at 157°.

By the action of PCl_5 on dinitro γ-dichloronaphthalene, ε-tetrachloronaphthalene is obtained, which crystallises in long white needles, melting at 180°, and is difficultly soluble in alcohol. P. P. B.

Derivatives of Naphthaquinone. By T. DIETT and V. MERZ (*Deut. Chem. Ges. Ber.*, x, 2034).—*Monobromnaphthalic acid*, $C_{10}H_4Br(OH)O_2$, results from the action of bromine on naphthalic acid, dissolved in boiling glacial acetic acid. It is a crystalline body, which forms well crystallised salts.

By an excess of bromine in the presence of iodine, higher brominated compounds are produced. Nitro-naphthalic acid was also prepared, but no particulars are given. T. C.

Derivatives of Flavopurpurin. By E. SCHUNCK and H. ROEMER (*Deut. Chem. Ges. Ber.*, x, 1821—1823).—The difference demonstrated by the authors (*Deut. Chem. Ges. Ber.*, ix, 678) to exist between flavopurpurin and isopurpurin, is also exhibited by various derivatives.

Diacetylflavopurpurin, $C_{14}H_6(C_2H_3O_2)_2O_5$, produced by boiling acetic anhydride with flavopurpin, crystallises from glacial acetic acid in gold plates, melting at 238°, and subliming at 125°. At the same time, more especially if the temperature at which the action takes place be 180—200°, *triacetylflavopurpurin*, $C_{14}H_5(C_2H_3O_2)_3O_5$, is obtained. It crystallises from glacial acetic acid in sulphur-yellow needles melting at 195—196°, and sublimes about 150°. Triacetylisopurpurin melts at 220—222°.

Dibenzoylflavopurpurin $C_{14}H_6(C_7H_5O)_2O_5$, is produced by the action of benzoyl chloride on flavopurpurin; from acetic acid it crystallises in concentrically grouped needles of pale yellow colour, and melting at 208—210°.

Tribromflavopurpurin, $C_{14}H_5Br_3O_5$, produced by the action of bromine on an acetic acid solution of flavopurpurin, crystallises in beautiful orange-yellow needles, melting at 284°. It is difficultly soluble in glacial acetic acid, but dissolves easily in caustic soda, with a colour approaching more nearly that of alizarin than flavopurpurin; this solution exhibits absorption-bands like those of alizarin, but weaker.

Flavopurpurin imparts to pure sulphuric acid a red-violet colour; isopurpurin a red brown. P. P. B.

Anthraquinone-, Oxyanthraquinone-, and Alizarin-Carbonic Acids. By W. Hämmerschlag (*Deut. Chem. Ges. Ber.*, xi, 82—90). —*Anthraquinone-carbonic acid.*—The author obtains this substance by boiling methylanthraquinone (a by-product in the manufacture of alizarin) with acetic and chromic acids. Its best solvent is glacial acetic acid, from which it crystallises in thin needles closely resembling anthraquinone, and melting at 280°. When carefully heated it sublimes, without decomposition, in long yellow needles, but it is easily converted into anthraquinone. The acid dissolves in sodium acetate and ammonium oxalate, and is not precipitated from the solutions by acetic acid.

Oxyanthraquinone-carbonic acid is produced by fusing the sodium salt of the preceding acid with sodium hydrate. It is deposited from the aqueous solution of the fused mass, on addition of hydrochloric acid, in orange-yellow flocks resembling alizarin, but, unlike that body, soluble in sodium acetate and ammonium oxalate. It melts at 260°. The formation of this acid is precisely analogous to the formation of alizarin from monoxyanthraquinone.

Alizarin-carbonic Acid.—Anthraquinone-carbonic acid when heated with sulphuric acid, yields a sulphonic acid which is converted by fusion with sodium hydrate, into dioxyanthraquinone-carbonic acid, $C_{15}H_8O_6$ (not into alizarin, as stated by Liebermann). This product is precipitated by hydrochloric acid from an aqueous solution of the fused mass in red flocks, which dissolve in sodium acetate, and melt at 305°. When cautiously heated it sublimes in red needles. It is converted into trimellitic acid by oxidation. J. R.

Benzerythrene. By G. Schultz (*Deut. Chem. Ges. Ber.*, xi, 95—96).—This name is applied by the author to a hydrocarbon obtained, amongst other products, by passing the vapour of benzene through a red-hot tube.

Benzerythrene is insoluble in water, and nearly insoluble in alcohol and boiling acetic acid, but is soluble in hot benzene, and crystallises therefrom in small, shining laminæ, which melt at 307—308°, and are highly electric. It dissolves in strong sulphuric acid, forming a green solution, which is not precipitated by water. It is soluble in cold strong nitric acid, which converts it into resinous nitro-compounds. The formula of the hydrocarbon deduced from analysis is $C_{24}H_{18}$, according to which it is an isomeride of triphenylbenzene. J. R.

Chemical and Physical Properties of Amber. By O. Helm (*Arch. Pharm.* [3], xi, 229—246).—Amber, the fossil resin of *Pinites succinifer*, is found in primary deposits on the coast of East Prussia. The amber-bearing stratum, which lies partly below the sea-level, partly above, is of a bluish-green colour, and consists of a coarse-grained sand, whose particles have a yellow coating; scattered amongst the sand are particles of mica and glauconite; and in this "blue earth" is found the amber, to the amount of 1 kilo. per 20 cubic feet. The pieces of amber found are generally weathered, but have retained their original shape, showing that the sea has had but little action on them. The author doubts that amber found in other countries, and which has evidently suffered more from the action of the sea, is of the same kind as that found in Prussia. The quality of amber varies, not only in its appearance, but also in its chemical composition, as well as its specific gravity. The specific gravity, as a rule, lies between 1·05 and 1·095; the sort known as "bone" is even lighter, and some sorts are lighter than water. The colour is far from constant, being of all shades of yellow and brown, some ambers from Sicily being green or violet-blue. The blue colour is due to ferric phosphate, and the "clouding" is due to water enclosed, as by boiling in oil the cloudiness disappears; the bone-like amber, however, does not contain water, and the appearance in this case is due to the fact that the amber is of different origin, containing a larger quantity of succinic acid, which is often in the free state. If light-coloured amber be exposed to the light for a long time, its surface becomes darker, and at the same time is found to be covered with innumerable fine fissures, but the whole may be flaked off, leaving beneath amber of the original colour. Of the ordinary yellow amber, about one-fifth is soluble in ether, alcohol, turpentine, or chloroform. Alcohol or ether extracts a little resin, but ether extracts a portion which is insoluble in alcohol. This resin melts at 146°, whereas that soluble in alcohol melts at 105°. Besides these resins, succinic acid and a bitumen are found, having the composition of ordinary laurel-camphor, $C_{10}H_{16}O$. The proportion of succinic acid is generally from 3 to 5 per cent., but some specimens contain as much as 8 per cent., the larger quantity occurring in the purer specimens.

The ash, which consists of silica, lime, ferric oxide, and sulphuric acid, varies from 0·08—0·12 per cent. Amber is easily distinguished from other resins, copal, for instance, by the succinic acid present, as well as by the melting point (about 300°). It is for the above reasons that the author considers that the "ambers" of other countries are not the same as that found in Prussia. Analyses and descriptions of other sorts are given.
E. W. P.

Note on the Wax contained in the Leaves of Ilex Paraguayensis. By P. N. Arata (*Gazzetta chimica italiana*, vii, 366—369).—When the solution obtained by exhausting *Ilex paraguayensis* with ether, or better with ether-alcohol, is treated with lime, filtered and evaporated, it leaves a fatty residue, resembling wax. It was freed from chlorophyll by treating its ethereal solution with animal charcoal; the ethereal solution was then agitated with water, to remove caffeine and other substances, and on evaporation left the pure waxy matter. When boiled with an aqueous solution of potassium hydrate, this was partly dissolved, leaving a residue soluble in ether, and much more butyraceous than the original substance. This was separated by treatment with alcohol into an insoluble portion, transparent, and of a yellow colour, and a soluble portion, which is white, and melts at 55°.

On neutralising with hydrochloric acid the alkaline solution obtained by saponification of the wax, a white precipitate is produced, which has acid properties, and is soluble in ether and in boiling alcohol. It melts at 105—110°, and has a density of ·8151 at 26°. From the results of the analyses it does not appear to belong to the acetic series, but its molecular weight is very high. The author proposes to call it *mateceric acid.* C. E. G.

The Constituents of Podophyllum Peltatum. By W. C. A. Busch (*Pharm. J. Trans.* [3], viii, 424).—The concentrated tincture was treated in the following manner :—

1. Mixed with water it yielded a turbid liquid and a light grey precipitate which was completely soluble in ether and in alkalis. Hydrochloric acid clarified the turbid liquid, producing a dark precipitate, which was nearly insoluble in ether, but readily soluble in alkalis.

2. Mixed with *acidulated water* it gave a precipitate, which was grey at the ordinary temperature, but deepened in colour at a higher temperature, and fused to a blackish-brown mass. The fused mass was precipitated as a greyish powder from its alcoholic solution by acidulated water. Alcohol and alkalis dissolve it, and ether partly so. It is soluble in hot water, but separates on cooling. Cold water dissolves but little of the resin; its aqueous solution is deprived of its colour by acids, but it is reproduced with a darker shade by alkalis.

3. On mixing it with *alum solution*, a bright yellow pulverulent precipitate was formed, which was darkened in colour by hot water, but did not fuse to a brown mass. The ash consisted chiefly of alumina. Hydrochloric acid removed most of the alumina from the resin.

4. *Ether* dissolves 60 per cent. of the officinal resin. This portion dissolved in alcohol, from which it was precipitated by water (light greyish); by alum solution (bright yellow); by alcoholic solution of lead acetate (orange yellow). All these precipitates are to some extent dissolved by hot water, but separate therefrom, for the most part, in the cold. The alum precipitate gave 1·25 per cent. ash. The portion soluble in ether contained nothing fixed.

The resin insoluble in ether was bitter, soluble in alcohol and in alkalis, and slightly so in water. Water, either pure or acidulated, gradually produced a grey precipitate, and solutions of alum and acetate of lead a darker but not a yellow precipitate. The bright yellow colour of the resin prepared with alum solution is therefore due only to the resin soluble in ether. The alkaline solutions of both resins were yellowish-brown in colour, and were not precipitated by acids from a dilute solution: after having been boiled with dilute hydrochloric acid they gave no indication of sugar by Trommer's test.

5. *Principles soluble in water.* The reddish filtrate from the precipitate thrown down by acidulated water was bitter, and was found to contain sugar by Trommer's test. On evaporation, the solution gave an amorphous bitter mass which was soluble in alcohol, but not crystallisable therefrom.

The filtrate from the alum precipitate was also bitter, and became ruby-red on concentration; a blackish, semi-fluid, bitter substance also separated, which proved to be insoluble in ether, carbon bisulphide, and in petroleum; it was soluble in alcohol and in warm water. It was not obtained in a crystalline form.

From the tincture of rhizome of podophyllum ether precipitates a dark-coloured mass, very bitter and containing sugar. A. J. C.

The Colour of Podophyllum Resin. By A. SENIER and A. J. G. LOWE (*Pharm. J. Trans.* [3], viii, 443).—Resin of podophyllum varies in colour from different shades of yellow to brown and green. Small proportions of water precipitate the resin in a much finer state of division, and of a much paler colour than the same proportions of acidulated water. The resin is deepened in colour by washing with hot water, and this is said by the authors to be due to the partial fusion and agglomeration of the particles. By suitable physical treatment and by varying the method of precipitation, the dark resin can be made darker, and the light-coloured resin lighter in colour: hence it is concluded that the whole cause of the difference in shade is due to the difference of comminution. Pale coloured resins are light in density, being composed of small particles; the dark resins are the contrary. The yellow colour of some specimens is due not to berberine, but to the acid colouring-matters of the rhizome, and may be heightened by the use of certain solutions, *e.g.*, alum-water, instead of acidulated water.

The variations of shade and colour do not affect the physiological action of podophyllum resin. A. J. C.

False Angostura Bark and Brucine. By W. A. SHENSTONE (*Pharm. J. Trans.* [3], viii, 445).—By a modification of Pelletier and Caventon's process the author has succeeded in obtaining strychnine from false angostura bark; the quantity in the bark is said to be small.

On account of the difficulty of separating strychnine from brucine, it is considered doubtful if the physiological action of pure brucine has ever been studied.

The presence of strychnine in brucine is best ascertained by acting on brucine with dilute nitric acid, then extracting with chloroform in presence of excess of potassic hydrate: the strychnine will be found in the chloroform residue.

Brucine can be purified from a small quantity of strychnine by crystallisation from water containing a few drops of acetic acid; but prolonged heating of the solution must be avoided. The mother-liquors resulting from this method of purification deposited, on spontaneous evaporation, a fine crystalline substance of a brown colour. It is said from its properties to be probably a new salt of brucine, though the base is not necessarily brucine. The filtrate from the crystals yielded a yellow deliquescent solid, which in some respects resembled Ludwig's igasuric acid.

When brucine is boiled for some time with a solution containing 1 per cent. of potassic hydrate, the solution becomes yellow, and yields by evaporation over sulphuric acid in a vacuum bright, pale yellow needles, which can be obtained white and silky by crystallisation from weak alcohol.

Brucine rapidly becomes more soluble by being boiled with distilled water. 15 grams ceased to crystallise in the cold after having been boiled for 48 hours with a litre of water. Continuing the boiling for 20 hours, the solution being still alkaline, there was obtained by evaporation a mass of a dirty brown substance, which was reddened by nitric acid, and was apparently readily soluble in alcohol, but less so in water. Brucine, therefore, readily undergoes alteration by being heated with pure water, or with slightly acid or alkaline water.

A. J. C.

Garrya Fremonti. By D. W. Ross (*Pharm. J. Trans.* [3], viii, 489).—From the leaves of the *Garrya fremonti* has been obtained a bitter substance, *garryin*, crystallising in cubes. From its reactions it is supposed to be an alkaloïd. It is soluble in water and in alcohol, gives a purple colour with sulphuric acid, and a colour changing from red to green with sulphuric acid and potassic chromate. Besides garryin the leaves contain resin, chlorophyll, tannin, and sugar. They yield 5 per cent. of ash. The root of this plant also contains garryin. A. J. C.

Colchicum Seed. By N. Rossenwasser (*Pharm. J. Trans.* [3], viii, 507).—The active principle, colchicin, has been obtained in a crystalline condition from its solutions in fusel oil and benzene. It is a neutral substance, and is not precipitated by the usual alkaloïd reagents until its aqueous solution has been acidified with certain acids. It is insoluble in ether, carbon bisulphide, and in petroleum benzin.

Colchicum seed contains 8·4 per cent. fixed oil, which is readily saponifiable, and after purification with charcoal and benzin is of a light brown colour, and has a bland taste. A. J. C.

Note on the "Saponin" of Sarsaparilla. By Prof. Flückiger (*Pharm. J. Trans.* [3], viii, 488).—The active principle of sarsaparilla has been obtained in a pure state, and its properties examined. It is suggested to retain the name first suggested by Galileo Pallotta, viz., *parillin*, instead of *smilacin*, which has been given to it by subsequent investigators.

The sarsaparilla root is extracted with alcohol, and the parillin precipitated either from an alcoholic solution by water, or from an aqueous solution by the addition of spirit. Prepared in this way, and after treatment with charcoal, the parillin is obtained in white scales or prisms, showing a double refraction in polarised light. The root yields about 0·19 per cent. pure parillin. Parillin is decidedly a neutral body.

Air-dried parillin contains water of crystallisation, which it loses at 100°. It melts at 210°; in cold water it is almost insoluble (1 part in 10,000). At 25° it dissolves in 25 parts 0·814 alcohol, and is much more soluble in boiling alcohol. It is soluble in chloroform, but will not recrystallise from that liquid. With strong sulphuric acid parillin gives a yellow solution, which becomes of a beautiful cherry-red at the edges, due to dehydration; 10 per cent. sulphuric acid causes parillin to become green when heated; kept in a water-bath it gradually acquires a fine red, and finally a brown colour. Phosphoric acid acts similarly, but gives more of a yellowish-green colour.

From the author's experiments, it is said to be evident that parillin is a glucoside, thus confirming the observation of Otten.

The *parigenin*, produced by the decomposition of parillin with dilute mineral acids, is insoluble in boiling water, so that it can be readily separated and washed. It is probable that the sugar separated is at least partially crystallisable.

When parillin is decomposed by dilute mineral acids, or when its chloroform solution containing alcohol is decomposed with hydrochloric acid gas, the liquid acquires a strong green fluorescence. The chloroform liquid is at first colourless, but suddenly becomes brown by transmitted light, and full green by reflected light. This behaviour, and the colour which parillin gives with dilute cold sulphuric acid, are the most delicate tests for parillin. The "saponin" of digitalis, and Schmiedeberg's digitonin, but not cyclamin, give this fluorescence. The mean of three analyses of one sample of parillin, which had been separated from parigenin by dissolving in water and reprecipitating with alcohol, gave—

	Per cent.	Theory for $C_{32}H_{53}O_{18}$ + $16CH_2$ = $C_{48}H_{85}O_{18}$.
C	60·4	60·7
H	9·0	9·0

The mean analysis of another sample gave—

	Per cent.	Theory for $C_{32}H_{53}O_{18}$ + $8CH_2$ = $C_{40}H_{69}O_{18}$.
C	56·95	57·3
H	8·28	8·2

From a comparison of the formula of saponin, $C_{32}H_{54}O_{18}$, as obtained by Rochleder from the saponin prepared from soap-root, with these results, and with that of the saponin found in digitalin by Schmiedeberg, the author considers it probable that there exists a series of saponins with the general formula $C_nH_{2n-10}O_{18}$.

Sapogenin and parigenin produced, together with sugar, when saponin and parillin are split up by acids, are closely allied; as also is cyclamiretin, resulting from the decomposition of cyclamin; possibly these bodies are likewise homologous. A. J. C.

Some Constituents of Hops. By E. G. BISSELL (*Pharm. J. Trans.* [3], viii, 508).—This paper consists of the details of experiments which were made to ascertain whether lupulin contains all the active principles of the hop. The doubts hitherto expressed on this point have not been confirmed by the author. The tannin of hop is said not to be either gallotannic or moritannic acid. A. J. C.

Chemistry of Vegetable Physiology and Agriculture.

The Albuminoïds and Amides contained in Potatoes. By E. SCHULZE and J. BARBIERI (*Landw. Versuchs-Stat.*, xxi, 63—92).—The nitrogen in potatoes exists not only in the form of albumin, but also as asparagine and solanine.

Asparagine was first detected in the potato by Vauquelin (*Gmelin's Handbuch der Chemie*, v, 360), and its presence therein was afterwards confirmed by Hirsch and Ludwig (*Gmelin's Supplementband*, 898), but the quantity was not determined. Solanine is present in small quantities only. Wolff found ·015 per cent., and Haaf 0·32 per cent. in potatoes taken up in May, while those examined in July contained ·042 per cent. (*Gmelin's Handbuch*, vii, 2071).

The authors found that the juice of potatoes contained only 37·2 r cent. of the total nitrogen in the form of coagulable albumin, and 2·8 per cent. in other combinations; this latter existed probably as "diosmirende Stoffe."

On dialysing potatoes for three days, 82 per cent. of the nitrogen, free from albumin, had passed into the diffusate, very little, if any, of the albumin passing through the membrane. Asparagine was found, but only to the extent of ·024 per cent. = ·0045 nitrogen. The potatoes examined contained ·4 per cent. of nitrogen in "diosmirende" combination. The asparagine contained but 1 per cent. of this nitrogen.

On the supposition that all the nitrogen in the insoluble portion of the potatoes was present as albumin, 65·2 per cent. was found to be coagulable. Kreusler obtained similar results, 60·1—73·2 per cent. Sachsse and Kormann's method answered well for the estimation of asparagine. Besides this substance, other amides were, however, present.

Five varieties of potatoes were examined, Nos. I and II having received a dressing of stable manure, Nos. III, IV, and V grown without any manure. The varieties were, Nos. I and II, Bodensprenger; No. III, Early Rose; No. IV, König der Frühen; No. V, Biscuit-Kartoffel.

An average sample of 2 kilos. from each variety was pulped and pressed, and kept in a closed vessel until the starch had settled, the juice then drawn off with a syphon, and filtered.

10 c.c. of each sample were heated with steam in "Hofmeister's" glass tubes, and used for the estimation of nitrogen. Another portion of the juice was freed from coagulable albumin by adding acetic acid and heating to 100°; after filtering, the nitrogen in the filtrate was determined. By subtracting this nitrogen from the total quantity, and multiplying by the constant 6·25, the percentage of albumin in the juice was obtained. The above liquid, freed from albumin and decolorised with animal charcoal, was heated with Millon's reagent, but in each case only a slight reaction was obtained. Heating with concentrated hydrochloric acid gave no colour; and on adding acetic acid and potassium ferrocyanide, no precipitate was formed. There-

fore only traces of noncoagulable albumin could be contained in the filtrate.

1. Asparagine was estimated in the juice free from albumin, by Sachsse and Kormann's method. The juice was mixed with sulphuric acid, and heated at 105° for two hours in a closed tube; the liquid was then neutralised with caustic potash, and shaken with sodium hypobromite. The results agreed well, notwithstanding that the quantity of acid used and the time of heating varied.

The juice, after heating with sulphuric acid, gave in the azotometer:—

	No. III.	No. IV.	No. V.
(*a*.)	·0697 p.c. N.	·0728 p.c. N.	·0527 p.c. N.
(*b*.)	·0700 „	·0742 „	·0532 „

This method gave no higher results than those which were obtained by boiling the juice with hydrochloric acid in an open vessel, for when No. III was thus examined it yielded in the azotometer ·0693 per cent. of nitrogen, which agrees closely with the former determinations.

2. The nitrogen was estimated in juice freed from coagulable albumin, by using nitrous acid instead of sodium hypobromite. The juice was heated with sulphuric acid, which decomposed the asparagine into ammonia and aspartic acid. The liquid could now contain only amido-acids, and not any amide-salts. By this method double the quantity of nitrogen was obtained, but by dividing this by 2, and then adding the nitrogen that has been converted into ammonium salts, good results were realised.

It does not answer to mix the juice directly with the nitrous acid, as too vigorous an action then takes place. It is always necessary to get rid of albuminoïds before boiling with hydrochloric or sulphuric acids, as they not only produce a precipitate, but also decompose albumin into amido-acids.

Results obtained by using the fresh juice:—

TABLE I.

No. of the potato.	*a*.	*b*.	*c*.	*d*.	*e*.	*f*.	*g*.
			Nitrogen obtained by shaking with hypobromite.				
	Total nitrogen in the juice.	Nitrogen in the juice free from albumin.	Before heating with sulphuric acid.	After heating with sulphuric acid.	Difference between *d* and *c*.	Nitrogen in the form of amido-acids.	Quantity obtained by adding *e* and *f*.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
I	0·3848	0·1878	0·0161	0·0667	0·0506	0·1207	0·1713
II	0·3975	0·1858	0·0154	0·0614	0·0460	0·1133	0·1593
III	0·3516	0·2307	0·0201	0·0699	0·0498	0·1657	0·2155
IV	0·3781	0·2273	0·0199	0·0735	0·0536	0·1430	0·1966
V	0·3748	0·1725	0·0182	0·0530	0·0348	0·1017	0·1365

As it was possible that there were other amides present which were decomposed by heating with sulphuric acid in the same manner as asparagine, this substance was extracted, obtained in the crystalline form, and then weighed. 200 c.c. of the juice free from albumin was concentrated to half its bulk in a water-bath, and then placed in a dialyser. After 24 hours the diffusate was removed, and fresh water added. The diffusates were then concentrated to a small bulk, when the asparagine crystallised out, and was filtered off, washed with water, dried at 100°, and weighed. The mother-liquor, on the addition of alcohol, gave a small quantity of asparagine, which was collected, recrystallised from water, and added to the former.

By comparing these results with those given in column *e*, in the last table, the following numbers were obtained:—

No. of the potato.	Asparagine contained in the juice.		Percentage of *b* calculated upon *a*.
	a. Estimated by Sachsse's method.	*b*. Estimated by crystallisation.	
	Per cent.	Per cent.	
I	0·477	0·325	68·1
II	0·434	0·280	64·6
III	0·470	0·377	80·2
IV	0·505	0·300	59·4
V	0·328	0·216	65·9
			Mean 67·6

67·6 per cent., therefore, of the asparagine, as given by Sachsse's process, could be obtained in the crystalline form. There is no doubt that some asparagine was lost in the mother-liquor.

Glutamic acid was carefully tested for, but its presence was not proved.

The nitrogen obtained by mixing the juice—without previous treatment with acid—with the hypobromite, existed in some undetermined form of combination. No ammonia (or but mere traces) could be detected in the juice.

If the nitrogen contained in the aspartic acid is subtracted from the quantity given in column *e*, Table I, the remainder will be that which is combined with amides that are not decomposed by heating with acids.

No difference was observed on treating the juice directly with nitrous acid before boiling with hydrochloric or sulphuric acids, as the following results show:—

10 c.c. of juice gave when mixed with nitrous acid—

Before heating with acid, 0·02496 gram nitrogen.
After „ „ 0·02464 „

By taking into consideration the above experiments, the nitrogen may be distributed between the albumin and amido-compounds as follows:—

The fresh juice contained:—

No. of the potato.	Albumin.			Asparagine.			Unknown amido-acid.		
	Per cent.			Per cent.			Per cent.		
I	1·231	containing	0·1970 N	0·477	containing	0·1012 N	?	containing	0·0701 N
II	1·323		0·2117 „	0·434		0·0920 „	?		0·0673 „
III	0·756		0·1209 „	0·470		0·0996 „	?		0·1159 „
IV	0·943		0·1508 „	0·505		0·1072 „	?		0·0894 „
V	1·264		0·2023 „	0·328		0·0696 „	?		0·0669 „

The quantity of nitrogen not combined with albumin or amides may be thus obtained:—

No. of the potato.	*a.* Total nitrogen in the juice.	*b.* Nitrogen in the form of albumin and amides.	Difference between *a* and *b*.	
			Percentage on the juice.	Percentage on the total nitrogen.
I	0·3848	0·3683	0·0165	4·3
II	0·3975	0·3710	0·0265	6·7
III	0·3516	0·3364	0·0152	4·3
IV	0·3781	0·3474	0·0307	8·1
V	0·3748	0·3388	0·0360	9·6
				Mean 6·6

An average, therefore, of 6·6 per cent. of nitrogen is contained in some unknown form of combination; no doubt a portion of it will be present as solanine.

Of the total nitrogen contained in the tubers, from 75·6—86 per cent. was found in the juice.

The following table gives the nitrogen in various combinations, as contained in the potatoes:—

No. of the potato.	Insoluble albumin.			Soluble albumin.			Asparagine.			Amido-acids of unknown composition.		
	Per cent.			Per cent.			Per cent.			Per cent.		
I	0·431	containing	0·069 N	0·895	containing	0·143 N	0·347	containing	0·074 N	?	containing	0·0510 N
II	0·288		0·046 „	0·980		0·157 „	0·321		0·068 „	?		0·0498 „
III	0·363		0·058 „	0·500		0·080 „	0·311		0·066 „	?		0·0768 „
IV	0·294		0·047 „	0·719		0·115 „	0·385		0·082 „	?		0·0682 „
V	0·544		0·087 „	0·919		0·147 „	0·239		0·051 „	?		0·0487 „

Or by dividing the *total* nitrogen between albumin and nonalbuminous substances, they obtained:—

	I.	II.	III.	IV.	V.	Mean percentage.
Albuminous substances ..	60·7	59·7	47·4	48·2	65·2	56·2
Non-albuminous ,, ..	39·3	40·3	52·6	51·8	35·0	43·8

The tubers were found, therefore, to contain nitrogen in the form of albumin and of amides—asparagine and amido-acids of unknown composition—the latter in considerable quantities: so that it is evidently incorrect to multiply the *total* nitrogen by the constant 6·25 when estimating the albuminoïds. This remark applies also to beetroot, the various kinds of turnips, and probably to other roots. It would be wrong, however, to say that the nitrogen in nonalbuminous forms of combination is of no value for animal food. It is conceivable indeed that certain amides may have a nutritive value approaching that of gelatin, which, though it cannot actually take the place of albumin in nutrition, nevertheless, when given in conjunction with albumin, retards the transformation of that substance, and thus economises it in the organism. It is not improbable that many amides act in a similar manner. R. C. W.

Respiration in the Ripening Fruits of Poppy and Rape. By A. Sabanin and N. Laskowsky (*Landw. Versuchs-Stat.* xxi, 194—199).—The authors have determined, by means of Mayer's apparatus, the amounts of oxygen consumed and carbon dioxide formed in poppies and rape at various stages of ripeness, employing for the purpose flowering-stems cut as short as possible. Their results are given in the following table, where the numbers in the first column indicate the order of ripeness, No. I in each case being a flowering-stem taken just after flowering, No. VII in the rape-series a stem bearing fully-ripened seed-pods, and No. VIII in the poppy-series an over-ripe capsule. The last four columns give the weight in milligrams of oxygen consumed and carbon dioxide formed in 24 hours by 1 gram of dry substance.

	Rape.		Poppies.	
	Oxygen.	CO_2.	Oxygen.	CO_2.
I	65	89	91	124
II	70	97	30	42
III	37	51	24	33
IV	14	19	24	33
V	16	22	23	31
VI	20	27	20	28
VII	12	16	15	21
VIII	—	—	8	11

It appears from these results that in both plants the consumption of oxygen falls off as the fruit ripens. From what is known of the disappearance of starch in these plants, the authors conclude that the maximum consumption of oxygen occurs just before the disappearance of starch. J. R.

On the Composition and the Ripening of Parmesan Cheese. By L. MANETTI and G. MUSSO (*Landw. Versuchs-Stat.*, xxi, 211—229).—This paper contains the results of analyses by the authors of several samples of ripe Parmesan cheese. It gives also the results of analyses by other chemists, and a table of the maximum and minimum amounts of the principal constituents of the cheese shown by the various analyses. According to this table, the composition of ripe Parmesan cheese varies between the following limits:—

Water	36·11	to	27·00	per cent.
Fat	24·10	,,	12·58	,,
Casein	44·10	,,	36·30	,,
Alcoholic extract	14·68	,,	7·71	,,
Aqueous ,,	9·80	,,	4·57	,,
Insoluble organic substance	30·06	,,	17·77	,,
Ash	7·18	,,	5·20	,,
Ammonia	0·39	,,	0·13	,,
Total acids (reckoned as lactic)	2·92	,,	1·68	,,
Nitrogen	7·83	,,	6·13	,,
Volatile acids	0·26	,,	0·11	,,

The rest of the paper is devoted to discussions of the conditions of manufacture, and the causes of ripening of cheese.

The authors believe that the ripening of cheese in general is due (1) to the operation of organised ferments, acting in the same manner as yeast, &c., and (2) to the operation of soluble ferments which act like pepsin, ptyalin, diastase, and other similar substances. The ripening of Parmesan cheese in particular is attributed to the latter of these causes mainly, the ferments by which it is brought about being either present in the milk of which the cheese is made, or introduced in rennet. The ripening of rich cheese, such as Roquefort, is attended by the decomposition both of nitrogenous constituents and of fats, the odour and piquant flavour of such cheese being due to fatty acids, free or combined with ammonia. In the ripening of Parmesan and other comparatively poor cheeses, however, decomposition is principally confined to albuminoïds, that of glycerides being very slight.

J. R.

Analytical Chemistry.

Notes on Water Analysis. By OTTO HEHNER (*Analyst*, January, 1878, p. 177).—In water analysis it is essential to examine the water in as fresh a condition as possible. Several samples of water, examined by the ammonia process, showed that, after an interval of eight months, the free ammonia had almost entirely disappeared, whilst the albuminoïd ammonia had either remained stationary or had diminished. Experiments were made with the view of ascertaining whether the change was due to animalcules, or other organisms, which had the power of acting upon or eating up the ammonia. During the first two days, the composition of a water containing albuminous urine, but to which no infusoria had been added, remained nearly the same. On the fourth day, the albuminoïd ammonia began to diminish, and on the fifth day had greatly fallen; whilst, on the other hand, the free ammonia had increased nearly threefold. The same water, plus infusoria, gave the same general results, viz., the free ammonia increased whilst the albuminous substances disappeared.

Free ammonia in its turn disappears in long-kept waters, and this fact explains the apparent difference existing between these results and those obtained in the case of the waters examined after a period of eight months.

It seems established that the amount of free and albuminoïd ammonia alters considerably in a few days.

In the estimation of free ammonia the addition of sodic carbonate to the water may be dispensed with in alkaline waters, and with such as contain either carbonates or chlorides of calcium and magnesium.

A. J. C.

Reduction of Nitro-compounds by Stannous Chloride: Estimation of NO_2. By H. Limpricht (*Deut. Chem. Ges. Ber.*, xi, 35—42).—When an organic nitro-compound is warmed with an excess of a solution of stannous chloride, the NO_2-group is reduced to NH_2, in accordance with the equation—

$$NO_2 + 3SnCl_2 + 6HCl = NH_2 + 3SnCl_4 + 2H_2O.$$

This reaction affords the means of estimating the amount of NO_2 in nitro-compounds. The author proceeds as follows:—

About 0·2 gram of the nitro-compound to be analysed is placed in a 100 c.c. flask with 10 c.c. of a solution of stannous chloride (150 grams of tin in a liter), and warmed therewith for a few minutes. After cooling, the flask is filled up to the mark with water.

Of this solution 10 c.c. diluted with water is mixed with a quantity of an alkaline liquid (180 grams of anhydrous soda and 240 grams of potassium and sodium tartrate in a liter) sufficient to redissolve the precipitate first formed; some starch-solution is added, and then standard iodine-solution is run in from a burette till a blue colour is produced.

Volatile nitro-compounds are best reduced by sealing them up in a tube with 10 c.c. of stannous chloride, and heating in the water-bath, with occasional agitation.

The strength of the solution of stannous chloride employed is determined beforehand by titration with the same alkaline liquid and iodine-solution. The difference between the amounts of iodine required before and after an experiment is, of course, equivalent to the quantity of NO_2 reduced or of stannous chloride oxidised.

The author gives numerous examples showing that the process is accurate. He states, however, that it is not equally satisfactory in all cases.

J. R.

Volumetric Methods for the Estimation of Hydroxylamine. By W. Meyeringh (*Deut. Chem. Ges. Ber.*, x, 1940—1947).—

Hydroxylamine may be estimated volumetrically by oxidation with the following reagents:—

1. *Iodine.*—The reaction is thus expressed—

$$2NH_3O + 2I_2 = N_2O + H_2O + 4HI.$$

To obtain constant results it is necessary that the hydriodic acid produced in the reaction should be neutralised as fast as it is formed. The author adds to a solution of hydroxylamine hydrochloride, a sufficient quantity of magnesia or sodium phosphate to prevent acidity, and a slight excess of iodine-solution of known strength, and titrates the excess of the latter with sodium thiosulphate.

2. *Ferric Sulphate.*—The reaction is as follows:—

$$2Fe_2(SO_4)_3 + 2NH_3O = 4FeSO_4 + 2H_2SO_4 + N_3O + H_2O.$$

Oxidation is complete only at 80—90°. An excess of ferric sulphate is employed, and the amount of ferrous salt formed is determined by titration with potassium permanganate.

3. *Fehling's Solution.*—Hydroxylamine reacts with cupric oxide in alkaline solution as follows:—

$$2NH_3O + 4CuO = N_2O + Cu_2O + 3H_2O.$$

The author drops the solution of hydroxylamine into the boiling copper-solution till the blue colour of the latter disappears.

As regards the accuracy of these methods, the numbers given by the author show that 1 mol. of hydroxylamine required for oxidation, by the first method, from 1·95 to 2·08 atoms of iodine; by the second method, from 0·97 to 1·01 atoms of oxygen; and by the third method, 1·01 atoms of oxygen. It was proved by the direct analysis that the gas evolved in all the reactions is nitrous oxide.

Hydroxylamine cannot be estimated by oxidation with potassium permanganate or chromic acid, since the reactions with these substances are not constant. J. R.

Method of Separating Quartz from Mixtures with Silicates.

By ERNST LAUFER (*Deut. Chem. Ges. Ber.*, xi, 60—61).—The method consists in fusing the pulverised minerals with microcosmic salt, which decomposes silicates, but does not affect quartz.

The fused mass, after cooling, is first boiled with dilute hydrochloric acid and thoroughly washed by decantation, and then treated with boiling soda-ley, which dissolves the silica from silicates, leaving pure quartz. J. R.

Method for the Analysis of Silicates by Means of Oxide of Lead.

By G. BONG (*Bull. Soc. Chim.* [2], xxix, 50—51).—The finely powdered mineral, after ignition to remove organic matter, is mixed with about three times its weight of pure red lead, and fused in a platinum crucible. The fused mass is digested with nitric acid, the solution evaporated to dryness, the residue treated with water, and the insoluble silica filtered from the solution, through which sulphuretted hydrogen is passed to remove the lead, after which the analysis is conducted in the ordinary manner.

The advantages of this method are twofold: first, the decomposition may be effected at a much lower temperature, and in a shorter time than by fusion with sodium carbonate, and secondly, it enables the alkalis to be estimated with much greater facility.

Nitrate of lead may be used instead of red lead, but if care be taken to remove all organic matter before fusion, there is no necessity for this substitution. L. T. O'S.

Analysis of Nickel and Bronze Money. By E. Busse (*Zeitschr. Annal. Chem.*, xvii, 53—64).—The author has tested several of the most generally adopted methods for the analysis of nickel and bronze coinage, and has selected those which require least time, and give good results.

Pure copper was obtained by electrolysis, and then thoroughly cleaned by boiling with water and weak soda. A little nitric acid was then added, and after again boiling in water, the copper was exposed to a red heat in a current of hydrogen.

Estimation of copper as cuprous sulphide, after precipitation by sulphuretted hydrogen.—A weighed quantity of pure copper was dissolved in nitric acid, 1 c.c. of concentrated sulphuric acid was added, and the solution evaporated to dryness; 200 c.c. of boiling water were then added, and sulphuretted hydrogen was passed through until the solution became cold. The copper sulphide precipitated settled quickly, and did not oxidise during the washing. The precipitate was dried at 100°, mixed with sulphur, and heated strongly in hydrogen.

0·4933 Cu gave—

$$0·6176\ Cu_2S = 0·49306\ Cu = 99·95\ \text{per cent.}$$

0·4877 Cu gave—

$$0·6109\ Cu_2S = 0·48769\ Cu = 99·99\quad ,,$$

Carbonic acid cannot be used instead of hydrogen.

0·5422 Cu gave—

$$0·67905\ Cu_2S\ \text{in hydrogen} = 0·54201\ Cu = 99·97\ \text{per cent.}$$

The precipitate with sulphur in carbonic acid gave—

$$0·682\ Cu_2S = 0·54444\ Cu = 100·41\ \text{per cent.}$$

and 0·5757 Cu gave—

$$0·7245\ Cu_2S = 0·57836\ Cu = 100·46\ \text{per cent.}$$

This latter mixed with sulphur again, and heated to redness in hydrogen gave—

$$0·7211\ Cu_2S = 0·57564\ Cu. = 99·99\ \text{per cent.}$$

Ulrici (*J. pr. Chem.*, cvii, 110) heats the sulphide in a porcelain crucible, allowing air to enter for a few seconds, now and then, and calculates the result as containing sulphur in the same proportion as cuprous sulphide. The author says that so many different compounds of sulphur, oxygen, and copper are present, that the weight gives no certain indication of the amount of contained copper.

Estimation as Thiocyanate, or as Cuprous Sulphide after previous precipitation as thiocyanate.—The solution of copper free from nitric acid is mixed with sulphurous acid, and precipitated with potassium thiocyanate. The precipitate is allowed to settle, and washed by decantation as long as the decanted solution gives a precipitate with nitrate of silver, then collected on a weighed filter, dried for 12 hours at 105° to 110°, and weighed.

0·4530 Cu gave 0·8667 $Cu_2S_2Cy_2$ = 0·4525 Cu = 99·86 per cent.
0·6560 Cu „ 1·2564 „ = 0·6556 Cu = 99·97 „
0·4000 Cu „ 0·7662 „ = 0·3999 Cu = 99·98 „
0·4424 Cu „ 0·8470 „ = 0·4421 Cu = 99·92 „

It can be seen that this method gives trustworthy results.

If it be preferred to weigh as cuprous sulphide, the thiocyanate is heated in a crucible, and then strewed with sulphur and raised to redness in a current of hydrogen. This gives a better result than the heating with sulphur before decomposing the thiocyanate as in the latter case a substance very hard to sublime is formed. (An analysis of this sublimate purified with water, alcohol, and carbon disulphide, gave 19·91 C, 13·18 N, 2·41 H, 64·5 S.

0·4282 Cu gave 0·5362 Cu_2S = 0·4280 Cu = 99·97 per cent.
0·5606 Cu „ 0·7015 „ = 0·5600 Cu = 99·90 „
0·4987 Cu „ 0·6243 „ = 0·4983 Cu = 99·95 „

Copper thiocyanate is almost insoluble in pure and acidulated water at the ordinary temperatures, but is soluble to some extent in boiling water.

0·4907 Cu as $Cu_2S_2Cy_2$, precipitated hot, and washed with boiling water, gave—

0·6128 Cu_2S = 0·4891 Cu = 99·68 per cent.

0·4265 Cu with 10 c.c. of concentrated sulphuric acid, precipitated with potassium thiocyanate, gave—

0·5338 Cu_2S = 0·4262 Cu = 99·92 per cent.

0·5013 Cu in presence of 10 c.c. of hydrochloric acid, gave—

0·627 Cu_2S = 3·5005 Cu = 99·83 per cent.

Acids, with the exception of nitric, do not influence the result, as can be seen by the above two experiments.

Instead of weighing the copper thiocyanate, a certain quantity of potassium thiocyanate can be used, and, after the precipitation the amount of unaltered potassium salt, estimated by Volhard's method (*J. pr. Chem.*, [2], ix, 217, or *Zeitschr. Anal. Chem.*, xiii, 171 and 242). In one experiment the gravimetric method gave 99·95, and the volumetric, 99·98 per cent. Another experiment gave 99·96 per cent., and 99·80 per cent.

Estimation of Nickel.—The ordinary cubes of nickel were dissolved in nitric acid, and evaporated with sulphuric acid. Sulphuretted hydrogen was then passed through the liquid, the excess boiled off, sodium hydrate added to one portion of the solution, and sodium hypochlorite to another. Both precipitates were well washed. The nickel solution remaining was then treated with the first precipitate until all iron was precipitated, and then with the latter, until no more cobalt remained in solution. The solution was then evaporated to crystallisation, and the nickel ultimately precipitated by electrolysis and purified by treatment with water and hydrochloric acid.

The chief point to be aimed at in the estimation of nickel is to learn the conditions under which the alkalis precipitate a pure nickel oxide.

0·1595 Ni dissolved in nitric acid was evaporated to dryness, and heated over a blowpipe. After every five minutes it was weighed, and at the fifth weighing was found constant. 0·2027 NiO = 0·1594 Ni = 99·98 per cent. After 12 hours' exposure to air, the weight had not altered, and this is true in case of oxide precipitated by alkalis. The process is as follows:—100 c.c. of a 10 per cent. soda solution is heated to boiling in a platinum evaporating basin; the nickel solution containing not more than 2 grams of nickel sulphate is then added; the liquid, after a little boiling, is diluted with water, the solution again heated, and the precipitate is allowed to settle, the solution decanted through a filter, and the precipitate well washed, dried, and heated to redness. The nickel oxide is then ground in an agate mortar, washed with water, and again heated.

(*a.*) In sulphuric acid solution, 0·368 Ni gave—

0·4671 NiO = 0·3675 Ni = 99·85 per cent.

(*b.*) Nitric acid solution, 0·4103 Ni gave—

0·5211 NiO = 0·4099 Ni = 99·92 per cent.

(*c.*) Sulphuric acid solution, containing an ammonium salt (2 grams ammonium thiocyanate), 0·4200 Ni gave—

0·5325 NiO = 0·4191 Ni or 99·89 per cent.

The results are not exact—

(1.) In case less soda or less concentrated soda is employed.

(2.) Even if precipitation be correct, when the washing before the first heating is carried too far, *e.g.*, till the alkaline salts are washed out.

1. Experiments showed that if dilute soda be used, a basic sulphate is precipitated, as well as the oxide. This gives a higher percentage after the first heating, and a second washing causes the basic sulphate to react on the nickel oxide, and form a normal and soluble sulphate; *e.g.*, after the first heating, 102·14 per cent. of Ni; after washing and second heating, 99·16 per cent.

2. By washing too much before the first heating, 99·79 per cent. of Ni was found, and the washings contained nickel.

Separation of Copper from Nickel.—The method of precipitating copper with potassium thiocyanate is best when one-fourth of its weight of nickel is present, as sulphuretted hydrogen carries down some nickel with the copper, whether the solution be concentrated or dilute, hot or cold. The following table gives results of precipitation by sulphuretted hydrogen:—

No.	Copper employed.	Acid.	Total volume.	Temperatures.	Cu_2S produced.	Calculated copper.	Per cent.
		Nitric.					
1	0·6410	10 c.c.	200 cc.	15°	0·8088	0·6457	100·73
2	0·7722	„	200 cc.	100	0·9749	0·7782	100·86
3	0·7077	„	400 cc.	15	0·8898	0·7102	100·34
4	0·7657	„	400 cc.	100	0·9625	0·7683	100·35
5	0·6787	15 c.c.	200 cc.	100	0·8535	0·6813	100·38
6	0·6751	20 c.c.	400 cc.	15	0·8478	0·6768	100·25
7	0·7026	30 c.c.	400	15	0·8824	0·7044	100·25
8	0·7348	30	400	15	0·9215	0·7356	100·11
		Concentrated sulphuric acid.					
9	0·6893	1 c.c.	200	15	0·8838	0·7056	102·37
10	0·6635	1 c.c.	200	100	0·8467	0·6759	101·87
11	0·6180	1 c.c.	400	100	0·7804	0·6230	100·80
12	0·6441	2 c.c.	200	100	0·8087	0·6455	100·22
13	0·7000	3	200	100	0·8779	0·7008	100·11

Weighed quantities of copper and nickel, amounting together to not over 1 gram, were dissolved in 10 c.c. nitric acid of 1·18 sp. gr. The solution was evaporated with 1 c.c. concentrated sulphuric acid, and the product dissolved in a little water. 50 c.c. of sulphurous acid, and 2 grams of potassium thiocyanate were then added. After twelve hours the precipitate was collected. The filtrate was evaporated with nitric acid (10 c.c.), and the nickel precipitated by the method above described.

Taken.

1. 0·6965 Cu + 0·2222 Ni.
2. 0·6441 Cu + 0·2027 „

Found.

No.	$Cu_2S_2Cy_2$.	Cu.	Cu_2S.	Cu.	Per cent. mean.	NiO.	Ni.	Per cent.
1	1·3336	0·6961	0·8724	0·6964	99·98	0·2821	0·2219	99·88
2	1·2340	0·6441	0·8065	0·6438	99·96	0·2577	0·2028	100·04

The plates from which the nickel coins were made are analysed in the same way, proper regard being paid to the presence of foreign matter, as sulphur, arsenic, iron, &c. Iron can be separated from the nickel oxide by dissolving and precipitating twice with ammonia.

Estimation of Tin in presence of Copper.—Four experiments were made with a bronze containing 4 per cent. of tin. About 1 gram of bronze was dissolved in varying quantities of nitric acid of sp. gr. 1·5, and 50 c.c. of boiling water were afterwards added.

The annexed tables show the results :—

No.	Substance taken.	Acid.	Water.	SnO_2.	Calculated tin.	Per cent.
1..........	1·0060	4 c.c.	5 c.c.	0·0531	0·04170	4·14
2..........	0·9970	5 c.c.	„	0·0520	0·04091	4·09
3..........	0·9991	6 c.c.	„	0·0511	0·04012	4·01
4..........	0·9965	6·5	„	0·0507	0·03988	4·00

The oxide of tin from 3 and 4 was white, and contained scarcely any trace of copper.

Another series with 6 c.c. of nitric acid of sp. gr. 1·5, and different proportions of water, gave :—

No.	Substance taken.	Acid.	Water.	SnO_2.	Tin calculated.	Per cent.
1..........	1·000	6 c.c.	3 c.c.	0·0508	0·03997	4·00
2..........	1·0054	„	4 „	0·0511	0·04020	3·99
3..........	1·0051	„	5 „	0·0520	0·04091	4·07
4..........	1·0010	„	6 „	0·5525	0·04130	4·13

1 and 2 were white, and contained only traces of Cu. From the above it can be seen that with 1 gram of substance 6 c.c. of acid and 3 of water should be employed. The use of boiling water for dilution causes the precipitate to settle more quickly.

Analysis of Bronze Money.—The tin and copper are separated as above mentioned, and then the zinc is precipitated as sulphide, washed, and heated with sulphur in hydrogen. To make the washing of the zinc sulphide easier, it is better to precipitate the copper with ammonium-, instead of potassium thiocyanate. Lead and arsenic may be present, but the evaporation with sulphuric acid before the precipitation of the copper leaves the lead as sulphate. Arsenic must be estimated in a fresh portion. S.

Potassium Xanthate as a means of determining quantitatively Carbon Disulphide, Copper, and Caustic Alkalis in presence of Alkaline Carbonates. By E. A. Grete (*Liebig's Annalen*, cxc, 211—221).—This method depends on the precipitation of cupric xanthate when a solution of a cupric salt is added to a solution containing potassium xanthate. The standard copper solution is prepared by dissolving 24·936 grams of copper sulphate in water; to this are added 200—250 grams of sodic-potassic tartrate (Rochelle salt), and then carbonate of soda, until the solution becomes blue; the whole is then made up to a litre. Thus 1 c.c. of this solution contains 0·006336 gram of copper, and corresponds to 0·03202 gram potassic xanthate.

In titrating a solution of potassic xanthate, the solution must be dilute, and should be gradually warmed, as at the ordinary temperature the complete precipitation takes some time; the end of the reaction is seen by an addition of copper solution producing no further precipitation in the solution, which is made clear by stirring.

To apply this method to determine free carbon disulphide, a portion of the latter body is weighed out in a thin glass bulb, which is broken under a small quantity of alcoholic potash, and thus converted directly into potassic xanthate; the excess of potash is neutralised with tartaric acid; and the solution, diluted if necessary, is titrated with the copper solution. In cases where the carbon disulphide is either impure, or mixed with air, gas, or soil, then it may either be distilled off and the vapours passed through a Will and Varrentrapp's apparatus containing a few c.c. of alcoholic potash, or the gas may be drawn through such an apparatus. The amount of potassic xanthate formed is then determined as before. If the material contains carbon disulphide combined, but yielding it on distillation with an acid, then the gases from the distillation are passed through an apparatus containing as before some alcoholic potash; the sulphides and thiocarbonates are removed from the resulting solution by a solution of lead acetate, an excess of the latter being avoided; and then the potassium xanthate determined by titration with copper solution. In applying this method to the determination of free alkali in presence of alkaline sulphides or carbonates, the material is triturated with alcohol and then carbon disulphide added. The solution is diluted with water, and the sulphides and thiocarbonates are removed as before by a solution of lead acetate, the resulting solution being then titrated with the copper solution. 1 c.c. of the copper solution is equivalent to 0·00782 gram K = 0·0422 gram KHO, or 0·0046 gram Na = 0·008 gram NaHO.

The amount of copper in a solution may be determined by titration with a standard solution of potassium xanthate. The weighed quantity of copper salt is dissolved in water; to this solution is added a large quantity of Rochelle salt, and if acid, it is neutralised by sodium carbonate. The approaching end of the reaction is seen by the copper solution becoming a bluish-green, when the potassium xanthate solution must be added in small quantities at a time until no further precipitate is formed.

The solution of potassium xanthate does not keep, and must therefore be standardised each day. P. P. B.

A Reaction of Citric Acid. By A. SABANIN and N. LASKOWSKY (*Zeitschr. Anal. Chem.*, xvii, 73—76).—The authors refer to papers on this reaction by Sarandinaki (*Deut. Chem. Ges. Ber.*, v, 1100), and by Kämmerer, in the same journal (viii, 736), and then proceed to describe the application to the testing for citric acid.

When citric acid and excess of ammonia (5 grams to 30 c.c.) are heated in sealed tubes at 120° for six hours, a yellow coloration is observed, and small crystals are formed. If the liquid on cooling be poured into an evaporating basin and allowed to stand for several hours, it becomes blue. The crystals disappear, and the colour becomes more intense the longer it stands. After several days the solution turns green, and ultimately becomes colourless again. The green solution appears blue by transmitted light, whilst the blue solution under the same circumstances exhibits great intensity of colour. If the solution be kept in the dark, the change in colour goes on slowly. In an atmosphere of carbonic acid there is no change. When the heating in the sealed tubes is continued for a long time, or the temperature raised to 150°, or when 10 grams of citric acid instead of 5 grams are added to the 30 c.c. of ammonia, the green product is produced directly. The coloration can be produced more quickly by placing the solution over the water-bath after it has been heated in the sealed tubes, but the resulting colour is not so deep.

If the citric acid and ammonia are heated above 160°, no coloration takes place. The authors have not yet separated the colouring matter.

The reaction occurs in presence of oxalic, citric, and malic acids, even when these acids are present in the proportion of 10 to 1 of citric acid. The only condition necessary is that 10 milligrams of citric acid be present in the solution. In presence of itaconic acid the reaction failed.

For the testing of citric acid in fruit-juices, the following plan is proposed. The juice is mixed with alcohol, left for some hours, and then filtered. Lead acetate is added in excess, the precipitate collected and washed, and ammonia is added in excess. The solution is then evaporated to get rid of ammonia, and sulphuretted hydrogen is added. The lead sulphide is filtered off, and the solution warmed, to get rid of the sulphuretted hydrogen. Barium acetate is then added in excess, and the precipitate and the liquid are heated together; and the precipitate is collected on the filter, washed, and decomposed with sulphuric acid. The supernatant liquid is then heated with ammonia in sealed tubes, as above stated.

The authors remark that the barium salt is not $(C_6H_5O_7)_4Ba_6 + 7H_2O$, but $(C_6H_5O_7)_2 Ba_3 + 5H_2O$. The former is precipitated only from nearly pure citric acid, so that the precipitation by barium is not a certain test of the presence of citric acid. By this test the authors found this acid in oranges, cranberries, and black currants. S.

Tests for Oil of Almonds. By J. D. Bieber (*Chem. Centr.*, 1878, p. 14).—The author finds that most oil of almonds is in reality nothing but peach-kernel oil. He has experimented on sweet as well as bitter almonds, new as well as old, and finds the reactions hold for Sicilian, Provence, and Berberice almonds.

Equal weights of *pure* concentrated sulphuric acid, red fuming nitric acid, and water, are mixed and allowed to cool. Five parts of oil mixed with one of acid mixture give—

Pure almond oil, a light yellowish-white liniment.

Peach-kernel oil becomes first peach bloom, and later dark orange.

Sesame oil, at first pale yellowish-red, and later dirty orange-red; and

Poppy and walnut oils, a somewhat whiter liniment than almond oil.

Pure nitric acid, sp. gr. 1·4, gives with—

Almond oil, pale yellowish liniment.

Peach-kernel oil, directly a red liniment.

Sesame oil, dirty greenish-yellow, and later a red mixture; and

Poppy and walnut oils, a perfectly white liniment.

5 per cent. of peach oil and sesame oil can be discovered in almond oil by the nitric-sulphuric acid method. If 10 per cent. of peach oil be added to almond oil, and the acid added, the mixture may be used as a colour test for estimating the amount in other samples. S.

The Coloration of Peppermint Oil by Chloral Hydrate. By M. DUNIN (*Arch. Pharm.* [3], viii, 481—510).—This paper contradicts an assertion made by C. Jehn, that peppermint oil is always coloured red or brown by chloral hydrate. Although the latter substance has, when pure, the property of colouring some peppermint oils brown, greenish, or reddish, it acquires this power to a much greater extent when it contains hydrochloric acid. W. R.

Distinctive Tests for Cinchona Alkaloïds. By R. GODEFFROY (*Arch. Pharm.* [3], viii, 515—521).—The tests to be described are intended to enable druggists to distinguish between the sulphates of the cinchona alkaloïds, which, as is well known, resemble each other very closely in appearance, taste, &c. The principle of the methods is to mix a drop of a saturated solution of the sulphate with a drop of a solution of potassium thiocyanate, and to observe the appearance under the microscope with a linear magnifying power of 110. To comprehend thoroughly the appearance of the crystals, reference to the cuts inserted in the original paper is necessary, but a description may prove of some service. Quinine sulphate shows small round globules like small starch granules, arranged in curved lines. When allowed to crystallise without addition of thiocyanate, quinine sulphate forms sheaf-like or fan-like bundles of needles. With thiocyanate conchinine (quinidine) sulphate forms crystals resembling club moss. Cinchonine sulphate assumes a form resembling stags' horns; and cinchonidine sulphate forms feathery crystals, arranged in stars or sheaf-like bundles. W. R.

Test for Elaterin. By D. LINDO (*Chem. News*, xxxvii, 35).—Elaterin dissolves in liquefied crystals of carbolic acid without production of colour, but the addition of two or three drops of concentrated sulphuric acid develops a beautiful carmine colour, which changes to orange, and after some time to scarlet. Alkalis discharge the colour. The test can be applied directly to some samples of elaterium of commerce (dried sediment of the juice), if they are reduced to fine powder. A. J. C.

Analysis of Butter Fat. By M. KRETZSCHMAR (*Deut. Chem. Ges. Ber.*, x, 2091—2095).—In Hehner and Angell's process for detecting the adulteration of butter (*Zeitschr. Anal. Chem.*, 1877, 145), the percentage of fatty acids insoluble in water is determined, and butter containing more than 88 per cent. of fatty acids insoluble in water is not considered genuine. The author examined several samples of butter of known purity by this method, and found that they contained 89·20 to 89·57 per cent. of insoluble fatty acids. The limit must, therefore, be raised from 88 to 90 per cent. In other respects this process yields satisfactory results.

Two samples of artificial butter contained 95·5 and 95·1 per cent. of insoluble fatty acids; two samples of lard contained 95·8 and 99·5 per cent.; castor-oil 95·90 per cent.; and the fat from a fresh human corpse 95·4—95·2 per cent. W. C. W.

Estimation of Sugar in Milk. By R. GSCHEIDLEN (*Pflüger's Archiv. f. Physiologie*, xvi, 131).—When milk is boiled with caustic soda, a red liquid is produced, and a yellowish-white coagulum; by filtering this through asbestos and comparing it with a similarly prepared solution containing a known amount of milk sugar, by the ordinary colorimetric processes, a close approximation to the amount of sugar present is readily obtained. Soda solution of 20 per cent. is added to the milk in equal volume, and the whole boiled for 2—3 minutes in each case: a longer time of boiling, 6 to 10 minutes, gives a darker shade. Instead of colorimetric determinations, spectroscopic observations may be made by Kerordt's method, the extinction-coefficient being determined once for all with a standard sugar solution.

Haidlen's process consists in evaporating to dryness with gypsum, treating with ether, and dissolving out the sugar from the residue by means of 85 per cent. alcohol; when due correction is made for the salts dissolved out, this method gives results comparable with those obtained by the above processes, or by means of Fehling's solution after removal of albuminoïds: on the other hand, the results obtained by the polarisation method are more irregular, as are also those given by the method of Boudet and Boussingault, viz., use of Fehling's solution without removal of albuminoïds.

Human milk contains from 3·07 to 4·42 per cent. of sugar during periods of from 2 to 130 hours after birth (5 cases examined). According to Brunner, upwards of 6 per cent. is formed at later periods. Simon found that less sugar is contained in human milk some time after the birth than just after; whilst Crusius found that cow's milk increases in sugar after calving, until a constant percentage is attained. C. R. A. W.

The Valuation of Vinegar. By C. JEHN (*Deut. Chem. Ges. Ber.*, x, 2108).—The strength of the vinegar is determined by measuring the volume of water which is displaced by the carbon dioxide evolved by the action of 10 c.c. of the sample, on sodium bicarbonate. To avoid calculations, the cylinders in which the water is measured may be so graduated as to represent the percentage of acetic acid.

W. C. W.

Wine Analyses. By DR. BUCHNER (*Dingl. polyt. J.*, ccxxvi, 531—533).—Chemists are often required to distinguish between natural and artificial wines. Analyses of good wines abound, but the inferior wines have been less investigated. The author has analysed a series of wines, in which the alcohol was determined by distillation, the extract by drying in a current of air at 105°, and the acid was estimated as tartaric acid.

White Wines.

	Alcohol.		Extract.	Acid.	Ash.
	Weight per cent.	Volume per cent.			
Marburg	5·8	7·2	1·86	0·7	0·12
"	7·9	9·9	1·4	0·7	0·14
Sausal	4·9	5·9	1·72	0·7	0·08
Windish Bücheln	5·6	7·0	1·60	0·8	0·13
" "	5·0	6·1	1·2	0·5	0·08
" "	7·09	8·9	4·4	0·8	0·16
" "	6·95	8·6	4·2	0·8	0·15
" "	7·37	9·1	1·35	0·75	0·11
Marburg	8·48	10·5	1·9	0·7	0·20
"	8·41	10·5	1·7	0·6	0·16
Radkersburg	9·2	11·4	1·4	0·8	0·11
Fünfkirchen	8·0	10·0	1·2	0·8	0·16
"	9·36	12·0	1·25	0·6	0·18
"	7·9	9·9	1·73	0·8	0·14
Suspected White Wines	3·4	4·3	1·2	0·6	0·05
	6·4	8·0	1·0	0·7	0·08
	4·81	6·0	1·0	0·7	0·07
	5·2	6·5	1·1	0·5	0·07

Red Wines.

	Alcohol.		Extract.	Acid.	Ash.
	Weight per cent.	Volume per cent.			
Tyrol	8·2	10·1	1·9	0·8	0·23
South Tyrol	8·13	10·0	1·6	0·9	0·28
Fünfkirchen	11·0	13·6	2·3	0·8	0·15
"	9·8	11·9	2·4	0·8	0·16
Sansal	6·4	8·0	1·89	0·8	0·12
Schilch (suspected)	9·7	12·0	0·60	0·45	0·05
Flask Wines:—					
Jerusalem White	15·58	19·0	1·7	0·8	0·14
Nierstein	10·54	13·0	2·1	0·8	0·25
Sexzard Red	9·78	11·9	2·4	0·6	0·18
"	9·8	11·9	1·4	0·8	0·19
Böslau	11·85	14·5	2·4	0·8	0·23
Menesch, residues from	11·23	13·9	24·0	1·1	0·22
Marsala	13·31	16·3	5·5	0·8	0·32

Comparison of the above numbers shows the existence of a certain relation between the alcohol, extract, and ash. According to Mohr, the ash seldom reaches 0·5 per cent., it varies from 0·11 to 0·6 per cent., according to Van Gokow, Diez, and Neubauer.

Too little ash and alcohol indicate dilution; normal alcohol with too little ash indicates dilution with water and addition of alcohol.

Besides the light wines, some better ones are given which confirm the conclusion that in most cases the relation between the alcohol and the ash will afford indications of the quality of the wine. Only in one case is the relation between ash and extract abnormal, whilst the relation between ash and alcohol is quite normal; this sample, being of the first pressing, may be looked upon as an artificial wine.

Experience shows that the addition of mineral constituents to artificial wines is not very easy to make. J. T.

Sulphuric Acid contained in Wines. By J. NESSLER (*Chem. Centr.*, 1877, 687).—The constituents of genuine wine such as alcohol, sugar, tartaric acid, glycerin, succinic acid, and different ethers, are cheap enough to be used for artificial wines, and such wines can be recognised only when an excess of any one ingredient is introduced. The author has found small quantities of free tartaric acid, but never free citric acid, in wines. Several manufacturers have been justly punished for adulterating their wines with sulphuric acid. Nevertheless, natural wines often contain sulphuric acid. In natural wine from Boder, the author found 0·03 to 0·06 p.c., and in French wines, 0·096, 0·008, and 0·116 p.c. Free sulphuric acid has not as yet been found in genuine wines, yet its existence is possible. To detect free sulphuric acid strips of white filter paper 30 or 40 cm. long, are dipped in the wine, which rises by capillary attraction, and as the sulphuric acid does not dry, it concentrates at the upper end. The paper is then heated to 100°, and if acid be present, the paper turns brown, and often becomes brittle. W. R.

Investigation of Beers, especially in relation to Acidity. By E. REICHARDT (*Arch. Pharm.* [3], viii, 522—532).—This paper is intended for those who propose to have beer analysed, as well as for analysts: (1.) For acidity, $\frac{1}{2}$ to 1 litre is necessary. The acidity is difficult to estimate by titration, for the natural colour of the beer masks the change of tint of litmus paper. Taste is the best guide; but microscopic examination is also of service. Alcoholic ferment consists of globular masses of various sizes, the larger of which are dotted over with minute specks. As acid fermentation sets in, these round masses change to elliptical, and finally to long fibres united to each other at each end. (2.) Alcohol, extractive matter, albumin, sugar, and glycerin, are determined in 1 litre of beer. The alcohol is estimated by distilling 200 cubic centimeters of beer, and collecting 65 cubic centimeters of the distillate; the specific gravity of which affords a correct indication of the strength. The residue in the retort is filtered through a large weighed filter, the insoluble portion consisting of albumin. The filtrate is evaporated to dryness, and heated to 100°. It consists of extractive matter. Sugar and bitter substances are dissolved out from this extract by digesting it with absolute alcohol; glycerin by evaporation to dryness with lime and subsequent treatment with alcohol, which on evaporation leaves pure glycerin. Ash is determined by igniting the residue. (3.) Foreign bitter substances are best detected by Dragendorff's method (this *Journal*, 1874, p. 818). (4.) The specific gravity is also determined.

W. R.

Examination of Hops. By W. E. PORTER (*Analyst*, Jan. 1878, p. 176).—The following results were obtained from fair samples of new hops (1877) by extraction with ether: F = fine; M, medium, and L, low, in quality.

	Moisture. per cent.	Oil, resin, and bitter principle. per cent.		Moisture. per cent.	Oil, resin, and bitter principle. per cent.
1. Worcester, F....	4·02	14·98	7. Bavaria, M ..	9·97	13·08
2. Spalt, F........	6·96	14·08	8. American, M..	7·87	12·63
3. East Kent, F....	6·15	13·60	9. Sussex, L.....	8·55	9·95
4. Worcester, M....	8·10	13·35	10. Sussex, L.....	9·87	9·23
5. Kent, M	8·20	13·27	11. Poperingho, L.	10·25	9·25
6. Sussex, M......	7·05	11·75	12. Worcester, L..	9·20	8·80

The ethereal residues from Nos. 1, 2 and 3 had a golden tint, all the others were of a greenish hue.

The tannin in hops is said to vary between 2 and 4·5 per cent.

No doubt hops which contain a good percentage of tannin have their value increased, as the tannin precipitates the mucilaginous matter in the beer; but the oil, resin, &c., must be of the most value.

A. J. C.

Examination of Flour. By M. DUNIN (*Arch. Pharm.* [3], viii, 513—515).—The flour, which was stated to be obtained from rye, was slightly yellow. On drying at 100°, it lost 14 p.c. of water, and when burnt, gave 2·415 p.c. of ash, almost entirely soluble in water. The usual insoluble adulterations of flour, gypsum, alum, &c., were therefore absent. Pure wheat or rye-flour contains only about 1 p.c. of ash; leguminous seed contains 3·2 p.c., and is strongly alkaline. The sample was therefore treated for legumin by stirring 100 grams with distilled water, and evaporating the liquid portion to one-fourth of its volume after allowing the starch to settle. The precipitate caused in this solution by acetic acid dissolved completely in ammonia. The starch, besides consisting of the usual forms of rye-meal starch, showed a number of elliptical, kidney-shaped, or globular grains, which were recognised as peculiar to *Phaseolus communis*, L.

W. R.

Technical Chemistry.

Etching on Glass by Electricity. By PLANTÉ (*Ann. Chem. Phys.* [5], xiii, 143—144).—The author has previously drawn attention to the fact that when an electric current is passed through saline solutions in glass vessels, platinum wire serving as electrodes, the glass is immediately attacked, and he therefore proposes the following method for etching on glass.

The surface of glass to be engraved is coated with a concentrated solution of potassium nitrate: and beneath the layer of liquid a platinum wire, connected with one of the poles of a battery, is stretched across the plate. With the other pole is connected another platinum wire, the whole of which, except the point, is insulated; with this the designs are drawn on the glass, which is engraved wherever the wire comes in contact with it, flashes of light being emitted at the same time.

The depth of engraving depends on the rate at which the platinum wire moves; the slower the rate the deeper the line. L. T. O'S.

Heating Power of Brown Coal. By GERLAND (*Chem. Centr.*, 1878—31).—The coal was dried in the air, and then burnt in pieces varying in size from a nut to pieces as large as two fists. Two experiments were made in each case, the results being as follows:—the coal was burnt first in a chemical furnace, and then in an ordinary iron furnace with two iron flues on which the boiler rested:—

Bohemian Coal.

	Amount of Coal consumed.	Amount of Water in Boiler.	Amount of Water at 0° converted by 1 lb. of Coal into Steam.	Ash.
	lbs.	lbs.		per cent.
In chemical furnace..	4·192	9·43	1·093	3·5
In iron furnace	12·379	9·795	0·071	—

Habichtswalder Coal.

	Amount of Coal consumed.	Amount of Water in Boiler.	Amount of Water at 0° converted by 1 lb. of Coal into Steam.	Ash.	Relation of Heating Power of Habichtswalder Coal to Bohemian.
	lbs.	lbs.		per cent.	
In chemical furnace........	6·947	7·716	0·821	3·8	0·75
In iron furnace	12·712	10·726	0·054	—	0·76

S.

A Gas Generator. By C. GRÖBE and F. LÜRMAN (German patent) (*Chem. Centr.*, 1878—32). The arrangement differs from others in the fact that the production of gas takes place in two separate chambers. In the generators at present in use the water, tarry matter, and olefines are expelled from the upper layers, and the combustion of the lower layers gives carbonic oxide.

The method described by the authors consists in first heating the fuel by the waste heat of furnaces, so that tarry and other matters are driven off, and then the resulting coke is burnt into carbonic oxide.

The generator consists of two retorts lying close to one another, and opening at the back into a tower, which is provided at the bottom with a grate. The retorts are kept red-hot by the waste heat of other furnaces, and as the fuel is pushed gradually through the retorts it undergoes destructive distillation. The coke falls in a red-hot state into the tower (Schact), and is there burnt into carbonic oxide. The draught is so regulated that the gases and carbonic oxide, tarry and other matter are drawn off together. In this way the tarry and other matter having to pass over the red-hot coke, the whole is converted into heat-giving gas. S.

New Explosives. By Dr. SCHWARZ (*Dingl. Polyt. J.*, ccxxvi, 512—517).—The author proposes certain mixtures containing sulphur and carbon in combination instead of in admixture only. He takes potassium xanthate, nitre, and charcoal (1) in the proportion of 160 : 404 : 24 for one mixture, and (2) in the proportion of 160 : 303 : 9 for a second mixture. An increase of nitre diminishes the action of the explosive. Ordinary gunpowder corresponds to potassium xanthate 40 parts, nitre 100 parts, and charcoal 6 parts, which is almost identical with the first mixture given above.

The ingredients well ground and mixed are pressed into cakes with a little alcohol, and then granulated. The power of the mixture depends somewhat on the size of the grains. Thus in a testing machine, in which fine sporting powder indicated 40° to 46°, coarse, medium, and fine grain of (1) gave 36°, 58°, and 72° respectively; whilst medium and fine grain of (2) gave 40° and 74° respectively. This powder burns no quicker than common powder, so that it can be used for shooting. It requires to be kept dry to prevent decomposition of the xanthate.

If the nitre be replaced by potassium chlorate, a more violent explosive results, which, moreover, can be exploded by striking upon iron.

More energetic, and probably more quickly burning, compounds are obtained by mixing potassium chlorate with potassium (*a*) phenolparasulphonate, 2·75 parts to 1; (*b*) phenolmetasulphonate, 2·75 to 1; (*c*) benzenemonosulphonate, 2·8 to 1; (*d*) benzoldisulphonate, 2 to 1; and lastly, with ammonium phenolsulphonate, 3 parts to 1. These mixtures easily explode on being struck upon iron. J. T.

Magnesia-preparation for Purifying Potable Waters. By E. BOHLIG (*Dingl. Polyt. J.*, ccxxvi, 527—530).—Burnt magnesia being almost insoluble in water, sufficient to serve for a considerable time can be placed in the purifying tanks. No check-test is necessary; it is only necessary to agitate the water vigorously on first filling the tank. All lime is precipitated as carbonate, and gypsum is replaced by easily soluble magnesium sulphate.

Anhydrous magnesia takes up water very slowly, but this must precede the absorption of carbonic acid. Ignited magnesia in coarse particles may lie for some time in the water without passing into hydrate; but as in practice a month's supply can be placed in the tanks, this is no disadvantage.

The presence of various salts, especially of the alkalis, prevents the complete precipitation of calcium carbonate; but the same holds good for other methods of treating water.

On first adding the magnesia the water does not become clear very readily, but the second tank-full of water becomes quite clear in 30 minutes after agitating.

Water containing gypsum without carbonates requires a magnesia containing carbonate; but a mixture of raw and ignited magnesite will not serve. The remark of Mitscherlich that "magnesite and gypsum decompose each other," holds good only for artificially prepared magnesium carbonate. A cheap way of preparing basic magnesium carbonate is desirable.

The magnesia-preparation proper consists of a mixture of ignited magnesite powder and precipitated magnesium carbonate, as it was first applied to water containing gypsum only.

Fischer, in a note following the above, doubts that all the magnesia comes into action, its particles becoming covered with the precipitate, and asserts that the method is not to be recommended. J. T.

Purification of the Greasy Waters from Surface Condensers. By HÉTET (*Ann. Chim. Phys.* [5], xiii, 29—40).—The water from the surface condensers used for feeding the boilers of engines generally contains a large proportion of oil, which is saponified by the steam, and the fatty acids set free attack the boilers considerably, and form incrustations on the sides. To prevent this the author proposes to add dilute lime-water to the water before it enters the boilers, whereby insoluble lime-soaps are formed which remain behind.

L. T. O'S.

Formation of Sulphuric Anhydride in the Roasting of Pyrites. By G. LUNGE and F. SALATHE (*Deut. Chem. Ges. Ber.*, x, 1824—1830). Pointing out the fact that previous investigators of this phenomenon have not avoided the error arising from the easy oxidation of sulphurous to sulphuric anhydride, the authors recommend that the gases produced by the combustion of pyrites in air should be passed through solutions containing a known quantity of a decinormal solution of iodine. They find indeed that, when sulphurous anhydride mixed with air is passed through a given quantity of decinormal iodine-solution till it is decolorised (the sulphuric acid thus formed being determined as $BaSO_4$), the sulphurous anhydride is oxidised entirely at the expense of the iodine.

When the gases from the combustion of pyrites in air are passed through iodine-solution, in an apparatus for a description of which the original paper must be consulted, the amount of sulphur, as determined from the iodine used, is always less than that calculated from the sulphuric acid determined as barium sulphate, showing that about 6 per cent. of the sulphur burns to sulphuric anhydride. If the gases of combustion are passed over heated ferric oxide, the amount of sulphur burning to sulphuric anhydride is increased to 16—18 per cent.

The authors think that their method might be used for investigations on the large scale, and observe that in such cases the oxygen in the gases from the roasters should be estimated eudiometrically, as the pyrogallic method is not sufficiently exact. P. P. B.

Separation of Phosphorus from Iron. By P. TUNNER (*Chem. Centr.*, 1878, 24—30).—The phosphorus found in iron comes from the ores as well as from the fuel and the fluxes. In earlier times, before the enormous development of the iron industry, great care was exercised in the choice of ores, fuel, and flux, and the result was that the question of phosphorus did not occupy so much attention as now. The production of cast-steel and iron in proportion to that of steel of cementation and of wrought-iron, and the high temperatures necessary to produce the former substances, has made the question of the presence of phosphorus one of great importance. The great heat of the furnaces causes the phosphoric acid to be separated and then reduced, the phosphorus entering the iron. The author then goes on to notice the labours of Siemens in the direction of producing iron free from phosphorus in the Towcester and Canadian works by improving the apparatus used in the manufacture. A good account is given in the reports of the Iron and Steel Institute Meeting of September, 1877. The iron is made in a rotary furnace, and is then shingled into cakes, about an inch in thickness. These cakes are cut up and formed into blooms, and then rolled into bars. These bars are equal to Swedish iron, though the ores are not of a high class. The cost is given at £5 5*s.* to £5 10*s.* per ton.

I. L. Bell seeks to get out the phosphorus by melting the iron in a bath of oxides.

According to this latter investigator the carbon and phosphorus in ordinary puddling are present in the following proportions in the different stages:—

	C.	P.
The pig contained per cent.	3·180	1·494
1st stage, after melting	2·830	0·913
2nd „ partly refined	2·800	0·582
3rd „ „ „	1·170	0·519
4th „ puddled iron	0·150	0·452

Another more searching investigation gave the following. The iron was cleaned of slag by fusion with alkalis:—

	C.	Si.	S.	P.
1. Pig iron, Clarence No. 4....	3·150	1·120	0·093	1·209
2. On being melted	3·013	0·019	0·032	0·409
3. 26 minutes after fusion	1·973	0·024	0·013	0·085
4. 31 „ „	0·970	0·000	0·013	0·078
5. 39 „ „	0·294	0·026	0·013	0·094
6. 45 „ „ (puddled iron)	0·102	0·065	0·019	0·151

A second trial to check this gave—

1. Pig iron as melted	1·516 P.
2. Coming to nature and previous to treatment with alkali	·230
3. Ready for balling	·105
4. No. 2 bar, 1½-inch square	·145

From the above it may be seen that in the beginning of the operation there is a notable decrease in the quantity of phosphorus, but that, towards the end, as the temperature rises, this element is reabsorbed. The importance of getting out the phosphorus before it can be reabsorbed in the puddling furnace need not be dwelt upon. Bell took pig-iron containing 3·637 per cent. of carbon and 1·351 phosphorus, and fused it with oxides of iron. Whilst the percentage of carbon decreased 11 per cent. the phosphorus decreased 91 per cent. The iron thus produced compared well with some of the best refined irons, as the following table will show:—

	Bell's process.	Bowling iron.
Phosphorus	0·109	0·380
Carbon	3·227	3·393
Silicon	0·015	0·130
Sulphur	0·008	0·024

The composition of the cinder before and after the purifying was:—

	Fe_2O.	FeO.	FeS.	MnO.	Al_2O_3.	CaO.
Before	15·72	67·96	0·94	0·80	1·33	1·67
After	2·93	63·79	1·67	1·52	1·52	1·64

	MgO.	SiO_2.	P_2O_5.	
Before	0·81	8·45	2·95	= 100·63
After........	0·85	18·24	8·36	= 100·52

	Metallic iron.	Silicon.	Phosphorus.
Before	64·45	3·94	1·16
After........	52·72	8·51	4·71

The extent of change can be seen from the following:—

	C.	Si.	S.	P.
Pig iron contained	3·405	1·493	0·70	1·238
Purified metal	2·665	·101	·028	·282
Diminution in original quantity	21 p. c.	92 p. c.	60 p. c.	77 p. c.

This experiment was not so successful as the first mentioned.

The following table shows the change in calcined Cleveland ironstone used in refining:—

	Fe_2O_3.	FeO.	FeS.	MnO.	Al_2O_3.
Before refining	16·40	40·53	0·60	0·89	11·07
After "	3·27	33·56	0·85	2·12	11·59

	CaO.	MgO.	SiO_2.	P_2O_5.	
Before refining	6·40	4·06	18·74	1·89	= 100·58
After "	6·61	4·39	34·70	3·65	= 100·74

	Metallic iron.	Silicon.	Phosphorus.
Before refining ..	43·01	8·74	0·82
After " ..	28·39	16·19	1·50

As a result of these experiments Bell is engaged in trials on a large scale. On an elevated platform a small cupola will be placed, in which the cinder or other form of oxide will be melted. From this the molten matter will be run into a vessel revolving on its centre, and the iron will then be introduced. S.

Metallurgical Notes. By SERGIUS KERN (*Chem. News*, xxxvii, 23).—*On certain Gold Alloys.*—The alloys were obtained by melting crude gold direct from the mines. They contained per cent.:—

	1.	2.	3.	4.	5.
Gold	99·46	99·280	98·50	94·20	96·75
Silver	0·52	0·640	1·48	5·76	3·17
Lead	traces	0·005	traces	0·01	0·01
Copper	0·01	0·070	0·01	0·01	0·06
Bismuth	0·01	0·005	0·02	—	—
Iron	—	—	—	traces	none

No. 2 could be hammered in the cold, but it fell to pieces when being forged in a heated condition. Specimen plates from these alloys tore easily, and were very brittle. Ingots were prepared from the alloys, which had been worked with nitric acid, and refined by cupellation. They showed no brittleness, forged well, and were free from lead, bismuth, and iron. These results confirm the experiments of Roberts as to the effect of lead (antimony) and bismuth, in imparting brittleness to gold alloys. Gold alloys which contained notable traces of arsenic showed no brittleness; but ·05 to ·08 per cent. of arsenic would prevent gold alloys being readily worked under the hammer.

A. J. C.

Composition of Flue-Dust from Furnaces. By BL. BRITTON (*Chem. Centr.*, 1877, 320).—The author gives the results of some years' researches on this subject in the following tabular form:—

	I. From blast furnace.	II. From puddling furnace.	III. From forge.
Ferrous oxide	1·51	3·08	1·18
Ferric oxide	20·21	33·29	41·00
Alumina	6·57	12·89	7·54
Lime	3·98	0·48	0·61
Magnesia	0·69	0·09	0·19
Manganous oxide	1·66	0·39	0·12
Zinc oxide	2·84	—	—
Copper oxide	0·06	—	—
Silica	36·00	40·69	38·99
Sulphuric acid	7·55	1·05	0·43
Phosphoric acid	0·94	3·55	2·98
Arsenic	0·38	—	—
Ferric chloride	0·03	—	—
Cyanogen	0·09	—	—
Potassium with a little sodium	16·61	—	—
Carbonic acid	0·59	—	—
Alkalis, &c., and loss	0·29	4·49	6·96
	100·00	100·00	100·00

C. F. C.

Paraffin Oils and their Action on Metals. By STEVENSON MACADAM (*Pharm. J. Trans.* [3], viii, 463).—Paraffin oil, which had been stored in a lead-lined cistern, had so acted upon the metal and held the lead in solution, that the wicks of the lamp were found to contain sufficient lead to leave a fine net of metallic lead when the wick was charred. In a series of experiments with oils of various qualities, originally free from lead, the oils were allowed to remain in contact for different periods of time. Mere contact with the lead communicated traces of lead to the oil; and after a week's contact, the oil became so highly charged with lead as to be unfit for ordinary combustion, owing to the encrusting of the wicks. Experiments were also made with other metals.

1. *Bright Lead.*—A few moments suffice to communicate the metal to the oil. In a day the oil begins to present a cloudy appearance, and, on washing with water, the latter, on settling, retains a milky appearance from the lead compound, which is apparently a basic salt, and has an alkaline re-action.

2. *Tarnished Lead with Unprotected Edges.*—Lead, in small sheets, with fresh-cut edges, exposes a large surface of tarnished metal with the natural skin of oxycarbonate, and a comparatively small surface of bright metal. Under these circumstances, the lead is not so readily acted upon; but in a couple of days the oil gets impregnated with lead compound, and is rendered unsuitable for illuminating purposes.

3. *Tarnished Lead with Protected Edges.*—The fresh-cut edges were protected by wax; the oil acts even less energetically. Traces may be found in the oil in an hour after exposure, but it takes a week before the oil is largely impregnated with lead.

4. *Tin.*—This metal is very slightly acted upon. In a month's time the amount of metal dissolved was very small, and was not sufficient to impede the combustion of the oil.

5. *Copper.*—The oil is not practically affected.

6. *Iron.*—Very slight action. In 10 days' contact the oil becomes deeper in colour, and throws down a ferruginous sediment. The oil is not materially injured as an illuminant.

7. *Zinc.*—This metal is sensibly acted upon, the oil retaining the zinc compound in solution and suspension. The paraffin oil is decidedly injured as a luminant.

8. *Tin Solder.*—The alloy of two parts tin and one part lead is acted upon by the oil, and the latter is injuriously affected.

9. *Tin soldered with Tin Solder* has the lead dissolved out from the solder by the paraffin oil. The quantity of lead so dissolved is not large, but is sufficient to influence the oil as a luminant.

10. *Tinned Copper* is not practically affected; traces of tin and copper are found in the oil after a month's contact.

11. *Tinned Iron.*—The action is very slight.

12. *Galvanized Iron* is readily acted upon, and the oil is sensibly injured. Instead of tin, copper, iron, or tinned copper and tinned iron, either of which may be safely employed for paraffin storage, it would be preferable to use vessels lined with enamel, such as the ordinary enamelled iron pots, which present absolutely no surface upon which the paraffin oil can act.

The power of action on metallic lead was found to differ materially in experiments made with other samples of paraffin oils. This difference of action was not traceable to impurity, but it is probably due to the various proportions of the hydrocarbons present. A. J. C.

Dyeing with Aniline-Black by means of Vanadium Salts. By HOMMEY (*Chem. Centr.*, 1877, 41).—The woollen fabrics are left for 20—30 minutes in a bath, containing, for every 1,000 grams of water, 80 grams of aniline hydrochloride, 40 grams of potassium chlorate, 0·1 gram of ammonium vanadate, and 5 to 10 grams of hydrochloric acid, the latter being required to neutralise the traces of alkali left in removing fatty matters. The goods are then passed through the priming machine, and hung in a warm place, and next day treated with potassium chromate, well washed and cleaned. Thick heavy cloths should be passed through the bath without the metallic salt, and then, after priming a second time, through a bath with addition of the vanadate. This process answers well for mixed fabrics of wool and cotton, or of silk and wool. If a weaker bath is used, the cotton becomes of a dark green, the wool of a faint unsightly mignonette shade. In the hot chrome-bath which follows, the cotton assumes a lively black, with a violet tinge, the wool yellowish-brown to olive; so that a very pretty double effect is produced at one operation. G. T. A.

Use of Precipitated Sulphur in Dyeing. By M. REIMANN (*Deut. Chem. Ges. Ber.*, x, 1958—1961).—The first attempts to employ aniline-green in wool-dyeing were attended with difficulty, owing to the fact that this colour, unlike all other aniline-colours, is not fixed by wool without some previous treatment. The devices adopted by the dyer were very unsatisfactory until it was accidentally discovered that wool which has been steeped in a solution of sodium thiosulphate acidified with hydrochloric acid, takes the dye readily. This discovery removed the whole difficulty. The author has made some experiments with the object of ascertaining the part played by the sulphur in this process, and has arrived at the conclusion that it acts simply as a porous substance, just as silica acts with other dyes. He finds that wool placed in an acidified solution of sodium thiosulphate speedily takes up the precipitated sulphur, and acquires a distinct yellow colour. The wool thus treated is not affected by carbon bisulphide; but when boiled with weak soda-ley, it loses the power of fixing aniline-green, the sulphur being removed by the action of the alkali. It is thus shown that the fixation of the colour is directly due to precipitated sulphur, which is not soluble in carbon bisulphide. The sulphur-process is now employed in dyeing wool with eosine and its derivatives. J. R.

General and Physical Chemistry.

The Dark Lines of the Solar Spectrum and the Constitution of the Sun. By A. CORNU (*Compt. rend.*, lxxxvi, 315—317). —The author having carefully compared the intensity of the absorption-bands of the solar spectrum with those of the lines given by incandescent metallic vapours, concludes that the element entering in the largest proportion into the composition of the outer envelope of the sun is the vapour of iron; next follow nickel and magnesium, then at some distance calcium, and in still smaller proportions aluminium, sodium, and hydrogen, finally traces of manganese, cobalt, titanium, chromium and tin have been observed. This, according to the author, would be the approximate list of elements volatilised on the sun's surface in the order of their quantity. He draws attention to the similarity between the composition of this part of the sun, and of that observed in meteorites, and concludes that the relative brilliancy of the absorption-bands of the solar spectrum may be explained by the action of an absorbing layer surrounding the sun having a composition analogous to that of volatilised meteorites. J. M. T.

Elements present in the Layer of the Sun's Atmosphere which produce the Inversion of the Spectral Lines. By N. LOCKYER (*Compt. rend.*, lxxxvi, 317—321).—Lockyer finds that besides the elements already proved by the researches of Kirchhoff, Angström and Thalèn to be present in the outer envelope of the sun, namely, Fe, Na, Ir, Ca, Mg, Ni, Ba, Cu, Cr, Co, H, Mn, Ti, Al, Zn, the following are also present: Sr, Pb, Cd, K, Co, Ur, Va, Pd, Mo, In, Li, Rb, Cs, Bi, Sn, La, Gl, Yt. These results are shown in a table which gives the approximate wave-lengths of the absorption-bands, the names of the observers by whom they were first observed, and their degrees of intensity.

The author has made a special study of the long lines in the green: the long thallium line has been photographed, but no corresponding absorption-band in the solar spectrum has been observed. Two long lines of silver were also photographed, but it is impossible to say at present if corresponding absorption-bands exist in the solar spectrum. J. M. T.

Spectrum produced by the Electric Spark in a Compressed Gas. By A. CAZIN (*Compt. rend.*, lxxxiv, 1151—1154).—It is well known that with a continually increasing pressure, the spectrum of a gas gradually alters, its lines steadily widening out, until at length they disappear altogether in a continuous spectrum. This phenomenon is easily explained, if we admit with the author that the illumination produced by the electric spark in a gas is due to solid as well as to gaseous particles; the solid particles which are derived from the electrodes and the walls of the containing vessel become more and more abundant as the pressure increases, their continuous spectrum augments in brilliancy, and they eventually overpower and render invisible the fainter linear spectrum of the gaseous particles.

With nitrogen at ordinary pressure, the channelled spaces and lines are at first distinctly visible; with an increase of pressure, the channels gradually fade out, the lines widen, and the continuous spectrum becomes more brilliant. At two atmospheres there are only six lines and five diffuse bands visible. At ten atmospheres only three lines proper to nitrogen can be seen, but the sodium line, which is not distinguishable under ordinary circumstances, has now become very distinct, a tolerably good proof that the sodium is derived from the glass walls of the containing vessel.

The spark becomes hazy towards 15 atmospheres, but the four above-mentioned lines are still visible on the continuous spectrum, together with some brilliant points which are due to platinum. An increase of pressure up to 40 atmospheres does not alter the appearance of the preceding spectrum.

When the pressure is removed, the spectrum assumes its ordinary aspect, but the sodium line remains persistent, and may even be made to pass from one electrode to the other, as when a sodium compound is electrolysed, by reversing the current.

The author has succeeded in photographing these results, and has registered several lines as belonging to nitrogen, which have not been before observed. Under one atmosphere pressure the nitrogen lines in the photograph extend across that portion of the image which is feebly illuminated by a continuous spectrum; upon this background they are defined with exquisite sharpness, as many as thirty being capable of measurement in a space of 3 mm.

At 8 atmospheres the lines are scarcely visible, but with care, they may still be seen as numerous and as well defined as before. The author proposes to photograph in like manner the complete spectra of all the elementary gases. J. W.

Fluorescence. By E. Lommel (*Ann. Phys. Chem.* [2], 113—125).—The author has previously described (*Pogg. Ann.*, clix, 514) certain bodies which, like chlorophyll, have the property of emitting fluorescent rays of higher refrangibility than the exciting rays. He arranges all fluorescent substances in three classes.

I. Bodies in which each homogeneous ray of the exciting light can produce the entire fluorescent spectrum:—

	Beginning of fluorescence with spectrum. Bunsen's scale.	Spectrum of the fluorescent light. Bunsen's scale.
Chlorophyll......	28	26—40
Naphthalene red..	41	27—60
Eosin	50	28—77
Uranium glass ...	75	35—86

and others.

The author was surprised to find that the oft-examined uranium glass does not follow Stokes' rule.

II. Bodies in which exciting rays produce only fluorescent rays of lower, or at the most, of equal refrangibility:—

	Beginning of fluorescence with spectrum. Bunsen's scale.	Spectrum of the fluorescent light. Bunsen's scale.
Sandarac	34	25—132
Diphenylamine ..	65	36—113
Uranium nitrate ..	87	31—97
Petroleum	110	33—149
Fluorspar	142	32—145

and numerous others.

III. Bodies whose fluorescence spectrum consists of one part corresponding with that given by bodies of the Class I, and another part corresponding with that given by bodies of Class II:—

Potassium manganate ..	28	*28—42;* 49—165
Litmus	44	*32—55;* 55—79

and others.

The figures in italics show the portions of the spectrum in which Stokes' law is not followed.

To the first and third classes belong strongly coloured substances having strong absorption-bands only.

To the second class belong substances which show a partial absorption of the more refrangible portions of the spectrum; the absorption-bands are shadows, so to speak; and the bodies are yellow, brown, or colourless.

By mixing substances of the first and second classes, fluorescent bodies of the third class can be produced. A mixture of two substances of the first class could be easily detected as such; but this does not hold for a mixture of two bodies of the second class, as the mixture would behave like a single substance of the same class.

J. T.

Refraction of Gases and Vapours. By M. MASCART (*Compt. rend.*, lxxxvi, 321—323).—The results of the author's experiments are that the comparison of the refraction of gases and vapours should take place at the lowest possible pressures at which these bodies may be considered as being perfect gases. All his experiments were made at a temperature as near 12° as possible, and the results directly compared with those obtained from air under the same circumstances. The following are his numerical results:—

	Refraction compared with that of air.
Chlorine	2·63
Bromine	3·85
Hydrogen chloride	1·52
„ bromide	1·95
„ iodide	3·10
„ cyanide	1·49
„ sulphide	2·12
Ammonia	1·29
Water	0·88
Phosphorus trichloride ..	5·93
Carbon bisulphide	5·05

The author hopes soon to give his results for certain organic substances, and to discuss the theoretical calculation of the refraction of compound bodies. J. M. T.

The Electrical Resistance of Selenium. By L. A. FORSSMANN (*Ann. Phys. Chem.* [2], ii, 513—521).—In his experiments, the author used bars of fused selenium 2 mm. in diam., the ends of which were softened by heat and welded on to charcoal points in order to ensure a good contact. By long heating in an air-bath the bar was made to conduct electricity. A rod thus prepared, and 2·5 cm. in length, was arranged in a wide brass tube with an opening in the side, so that the selenium could be exposed to light or placed in complete darkness. The current was produced by several Meidinger's elements, and the strength observed by means of a galvanometer.

It was found, contrary to the results of Siemens and Adams (*Pogg. Ann.*, cl, 333; clix, 117, 621), that the intensity of the current is proportional to the number of elements, so that it obeys Ohm's law; and this was the case whether the selenium was exposed to the action of light or not.

The conductivity of selenium is nearly doubled by exposure to diffused daylight, whilst direct sunlight exercised a still more powerful influence. This influence appears to be two-fold, one instantaneous, the other gradual, so that the needle only attains its position of equilibrium after some minutes. In daylight, a permanent position of equilibrium could rarely be obtained, for a small change in the amount of cloud, at once produced a variation in the intensity of the current. The intensity increases in a very slow progression as the distance of the source of light diminishes.

The influence of a non-luminous flame is very small, thus confirming the results obtained by Adams; from this it might appear that the luminous part of the spectrum exercises the greatest influence, and that rays of a greater or less refrangibility produce a smaller effect, but it was found that when the increase in the intensity of the current produced by direct daylight was 43, that by yellow light was 40, by red 39, by blue 34, and by green 18; the increase in conductivity is therefore much smaller when the light has passed through green glass than through glass of any other colour. Consequently the effect is at a minimum in the green part of the spectrum, and increases on both sides.

It was also found that light, after passing through various coloured liquids, influenced the conductivity of selenium in a very different degree. A solution of a copper salt, although it transmits a great part of the visible spectrum, diminishes the intensity of the current almost to the same extent as complete darkness. Sulphuric acid coloured with selenium, which was far less transparent than the copper solution, produced almost as great an increase as direct light, as did also chameleon solution. Nickel salts and indigo solution diminished the intensity of the current, and the latter, when sufficiently concentrated, produced the same results as complete darkness.

From the above, the author concludes that the changes in the resistance of selenium are due to vibrations of a different order, if not of a different kind, to those which produce light, heat, or chemical activity. The possible influence of longitudinal vibrations must not be overlooked. After a bar of selenium has been exposed some time to light which has passed through the solution of a copper salt, the strength of the current rises very quickly above its normal intensity in direct light, if the copper solution be removed out of the path of the rays. By using a selenium solution, the opposite phenomenon takes place. To explain this, we may assume that the vibrations transmitted through cupric chloride tend to produce a new position of equilibrium among the molecules, which is strained, and therefore unstable; so that when the selenium bar is removed from the solution, and the tension ceases, a new position of equilibrium is taken up lying on the opposite side of that produced by direct light, although after some time the normal state is again attained. When the rays from a lamp are transmitted through a selenium solution, resistance is smaller than in direct light. This can be explained in one of two ways; either there are rays which produce a diminution of conductivity and are absorbed by the solution, or the passage of the rays through the liquid converts indifferent into active rays: a phenomenon analogous to fluorescence. T. C.

The Electric Conductivity of Selenium. By W. SIEMENS (*Ann. Chim. Phys.* [2], ii, 521—550).—As no success attended efforts to prove that bodies other than selenium underwent a change in their conductivity by the action of light, this phenomenon was considered to be intimately connected with the special properties of selenium. Börnstein, however, has found that an increase in the conductivity by the action of light is not limited to selenium, but occurs likewise with tellurium, platinum, gold, and silver.

Now if the increase in the conductivity of the illumined surface be dependent on the specific conductivity of the substance, then an increase in the conductivity of a thin metallic plate of silver must be easily recognised, since silver conducts 240,000 times better than selenium. It is quite different, however, if the increase in the conductivity occasioned by light bears no simple relation to the specific conductivity, and if, with Börnstein, we assume that a superficial conducting layer is produced by the action of light, for under these circumstances good conductors may conduct no better than the surface of selenium. As the conductivity of the surface can be measured only as an increase in the conductivity of the metal, and as we cannot diminish the thickness of the plate beyond a certain point, we soon arrive, even with metals which are good conductors, at a limit beyond which measurements are impossible, even with the most delicate instruments.

The author denies that the action of light produces on all metals such a superficial conducting layer as assumed by Börnstein, not on account of his own negative results, but from the fact that the sensibility of selenium to light is dependent to a very great degree on its purity and molecular condition, the slightest contamination with other elements greatly diminishing its sensibility to light; this sensibility is also considerably affected if the light be too strong, or by excessive cold or heat, even if no essential change takes place in the specific conductivity of the selenium.

The sensibility of tellurium to light would seem very probable, as shown by Adams, and also on account of its close relationship to selenium, nevertheless the author was unable to detect any evidence of it.

The selenium photometer gives, without any special care, comparative results sufficiently exact for technical purposes, but the dependence of the conductivity of selenium on too many uncontrollable factors prevents a photometer being constructed with selenium for measuring directly the intensity of light. Thus, the duration of the exposure has considerable influence. With Modification I of the metalloïd, a continuous illumination causes a constant increase in the conductivity; whilst with Modification II, the maximum is reached in a much shorter time, and afterwards decreases, first quickly, and then gradually slower. These phenomena occur, too, in a very different degree with different samples of selenium. The more the selenium has been prevented from becoming heated above 100° C. in its change from the amorphous to the crystalline state, the lower is its conductivity, and the more slowly does it increase with the duration of the light.

The fact that light increases the conductivity of selenium cannot be ascribed to a new property of light, for this would be admissible only if the special properties of selenium, or the known chemical action of light, were insufficient to account for it. As the author has previously pointed out, crystalline and amorphous selenium may be considered as allotropic modifications of the hypothetical metallic selenium, *i.e.*, selenium free from latent heat. If amorphous selenium be heated to 200° C., instead of 100°, it gives up more latent heat than at the latter temperature, and on cooling conducts electricity like a metal, *i.e.*, in such a way that the conductivity diminishes with the rise of temperature, whilst that of crystalline selenium (prepared at 100°), like that of carbon, increases with the temperature. Therefore the former, termed by the author Modification II, conducts very much better than the latter (Modification I). Modification I may be looked upon as a mixture of crystalline and metallic selenium; a complete conversion into metallic selenium is not possible, as the latter is not stable in the pure state at the ordinary temperature. A similar behaviour is exhibited by ozone, which, according to the author, is probably an allotropic modification of oxygen free from latent heat, and may therefore be considered as metallic oxygen. By means of the above theory, the action of light on selenium may be explained. The light rays, which fall on the surface of the selenium and penetrate to a certain but very small depth, have an influence similar to that produced by an elevated temperature; they reduce the crystalline selenium to the metallic state, and therefore render it a very much better conductor. On the illumination ceasing, the metallic surface of the selenium returns to the crystalline condition, as the metallic state is stable only under the action of light, or at a high temperature. To explain the phenomenon of the decreasing conductivity produced when the light acts continuously, we must assume that the crystalline modification is more transparent than the metallic, in which case the light at the commencement penetrates to greater depths, and changes the badly conducting crystalline into the good conducting metallic modification, but as soon as the surface has become covered with a metallic layer; the latter acts as a screen, preventing the light from penetrating so deeply, and thus allows the metallic molecules beneath to return to the crystalline state.

The author confirms Sale's statement, that the action of light commences only with the visible violet rays, and then rises pretty regularly to the red, but disappears beyond the ultra-red. Attempts to construct a scale of the illuminating values of different coloured lights, which exercise on selenium an equal light action, were unsuccessful.

T. C.

The Electrolytic Conductivity of Solid Salts. By T. GROSS (*Chem. Centr.*, 1878, 33—35).—Some of the salts were examined as crystals, and others as compact masses formed by fusion; they were kept dry during the experiment by the presence of phosphoric anhydride. Mercury electrodes were employed. Copper sulphate conducted the current until the mercury sulphate formed at the positive electrode prevented the current passing.

Many other salts behave similarly, but some are non-conductors, or become conductors only when heated. Some salt-solutions, after freezing, passed the current, but others did not. J. T.

The Contact Theory of Voltaic Action. By W. E. AYRTON and J. PERRY (*Phil. Mag.* [5], v, 219—222).—A note claiming priority in this matter, with reference to a paper by Clifton, "On the Difference of Potential produced by the Contact of Different Substances," communicated to the Royal Society in May, 1877, and also containing some critical remarks on Professor Clifton's paper.

M. M. P. M.

Hydrates of the Hydracids. By M. BERTHELOT (*Compt. rend.*, lxxxvi, 279—283).—The author describes the following hydrates, namely:—

$HCl + 2H_2O$, existing as liquid and solid, the latter melting at —18°. During its formation in the liquid state 11·62 th.-u. are disengaged, and in the solid state, 14·1 th.-u.

$HBr + 2H_2O$ also exists as liquid and solid, and the heat disengaged during its formation in the liquid state = 14·2 th.-u. The crystals melt at —11°.

Such hydrates play an essential part in the decomposition of those metallic sulphides which are attacked only by concentrated hydrochloric acid. They are analogous to the hydrate, $HNO_3 + 2H_2O$, formed, when nitric acid vapour is passed into water, with disengagement at 12·2 th.-u.

The heat disengaged in the formation of the hydrates, $HI + 3H_2O$, $HCl + 3H_2O$, $HBr + 3H_2O$, is 15·6, 13·6, and 16·2 th.-u. respectively, but there is nothing to indicate that they are definite compounds. The hydrates analogous to those of barium, $Ba(HO)_2 + 9H_2O$, and strontium, $Sr(HO)_2 + 9H_2O$, are:—

$HBr + 4·5\ H_2O$, during the formation of which 17·5 th.-u. are evolved; and

$HI + 4\cdot5\ H_2O$, during the formation of which 17 th.-u. are evolved;

These hydrates, from a study of their thermic curves and the tensions of their solutions, would appear to be definite.

$HCl + 6\cdot5\ H_2O$ corresponds nearly with the limit at which alkaline chlorides dissolved in concentrated hydrochloric acid are precipitated; and also at which the action of hydrochloric acid on the sulphides of antimony and silver ceases. The heat disengaged during its formation = 14 th.-u.

A corresponding hydrate of hydriodic acid is probably formed, as it corresponds with the limit of the action on sulphurous acid, and also with that of the action of sulphuretted hydrogen on iodine dissolved in hydriodic acid.

There are also indications that a hydrate of nitric acid having a similar composition exists. L. T. O'S.

Ebullition of Superposed Liquids. By D. GERNEZ (*Compt. rend.*, lxxxvi, 472—475).—After a minute description of the method employed and precautions necessary in conducting the experiments, the author gives the following statement; that superimposed liquids, having no chemical action upon one another, boil at the same temperature as that at which the sum of the maximum tensions of the vapours of the two liquids is equal to the pressure. He experimented with the following mixtures:—

	Boiling temperature.	Sum of the maximum tensions of the two vapours at the boiling temperature.	Excess of pressure.	Pressure.
Carbon bisulphide and water	43·68°	766·64	1·29	765·35
Carbon chloride and water	66·17°	747·36	1·91	745·45
Benzene and water	69·43°	765·92	1·48	764·44

J. M. T.

A New Specific Gravity Apparatus. By M. F. PISANI (*Compt. rend.*, lxxxvi, 350—352).—This consists of a glass vessel of about 5 c.c. capacity, closed with a perforated stopper, like an ordinary specific gravity bottle. To the side of the vessel is joined a tube, coming off at an angle of 45°, about 25 cm. long, and 4 mm. internal diameter, and graduated in 50ths of a c.c. The vessel is filled with water, the level of which is read off in the tube held vertically, the finger being held over the hole in the stopper. 2 or 3 grams of a mineral are then placed in the flask, the stopper is replaced, care being taken to lose no water, and the level is again read off in the graduated tube, held vertically as before. The difference in the two readings gives the volume of the mineral taken. J. T.

Vapour-densities. By L. TROOST (*Compt. rend.*, lxxxvi, 331—332).—The vapour-density of acetic acid at 120°, and under a slight pressure, corresponds to 2 vols. of the vapour, from which it follows that the greater vapour-density observed by Cahours at its boiling point is due to a rapid change of the coefficient of expansion of the vapour at that temperature. Nitric oxide at 22°, and under slight pressure, has a vapour density corresponding to 2 vols. From observations by the author at 360—440°, he believes that the abnormal vapour-density of sulphur vapour is due to a polymeric condensation of the molecules of the substance. L. T. O'S.

Some Specific Gravity Determinations. By F. W. CLARKE (*Am. J. of Sci.* [3], xv, 281—286).—The determinations of the density of the salts given in this paper were done by students, the weighings having been made in benzene, but the numbers all refer to water at its maximum density as unity.

BaI_2O_6 .... = 5·2179, 5·1853, 5·2855 at 18°.
$AgIO_3$.................. = 5·4023 at 16·5°; after recrystallisation from ammonia, 5·6475 at 14·5°.
PbI_2O_6.................. = 6·1783 at 19°; 6·1322 at 21°.
NH_4IO_3 .... = 3·3085 at 21°; 3·3372 at 12·5°.
CdI_2.................... = 5·9857 at 12°; 5·9738 at 13·5°.
BiI_3.................... = 5·9225 at 16°; 5·8813 at 17·5°.
$K_2NiCy_4H_2O$ .... = 1·875 at 11°; 1·871 at 14·5°.
$K_2PtCy_43H_2O$............ = 2·5241 at 13°; 2·4548 at 16°. Crystals slightly moist.
NH_4CyS .... = 1·299 and 1·316 at 13°.
$K_6CrCy_{12}S_{12}8H_2O$ .... = 1·7051 at 17·5°; 1·7107 at 16°.
$K_2PtCy_6S_6$ .... = 2·370 at 19°; 2·342 at 18°.
Sodium nitroprusside .... = 1·6869 at 25°.
$NiN_2O_66H_2O$ .... = 2·065 at 14°; 2·037 at 22°.
$ZnN_2O_66H_2O$ .... = 2·063 at 13°; 2·067 at 15°.
$CdN_2O_64H_2O$ .... = 2·450 at 14°; 2·460 at 20°.
$BiN_2O_65H_2O$ .... = 2·823 at 13°.
$KBrO_3$.................. = 3·323 at 19°.
$AgBrO_3$ .... = 5·1983 at 16°.
$BaBr_2O_6$ .... = 4·0395 at 17°.
CaS_2O_3.................. = 1·8715 at 13·5°.
$SrS_2O_36H_2O$ .... = 2·1566 at 17°.
$BaS_2O_3H_2O$.............. = 3·4461 at 16°.
$BaP_2H_4O_4H_2O$............ = 2·8718 at 10°.
$MgP_2H_4O_46H_2O$ .... = 1·5886 at 12·5°.
$NaPO_3$.................. = 2·4756 at 19·5°.
KPO_3 .... = 2·2639 at 14·5°.
Na_2WO_4 .... = 4·1743 at 20·5°.
$Na_2WO_42H_2O$............ = 3·2588 at 17·5°.
$BaWO_4$.................. = 5·0035 at 13·5°.
$NiWO_4$.................. = 6·8846 at 20·5°.
$BaMoO_4$.................. = 4·6589 at 17·5°.

$SrMoO_4$ .... = 4·1554 at 20·5°.
Na_3PO_4 .... = 2·5111 at 12°.
$Na_4P_2O_7 10H_2O$ .... = 1·7726 at 21°.
$MgCrO_4 7H_2O$ .... = 1·7613 at 16°; at 130° 6 molecules of water go off; the 7th molecule cannot be driven off without decomposing the salt.
$(NH_4)_2CrO_4$ .... = 1·9138 at 12°.
$(NH_4)_2Cr_2O_7$ .... = 2·1223 at 16°.
Na_2CrO_4 .... = 2·7358 at 12°.
$(NH_4)_2Mg(CrO_4)_2.6H_2O$.... = 1·8278 at 16°.
$K_2Mg(CrO_4)_2H_2O$ .... = 2·5804 at 19°.
Cr_2Cl_6 (well crystallised) .. = 2·3572 at 17·5; 2·3766 at 16·5; 2·349 at 20°.

The molecular volumes of these chromates are almost identical with those of the corresponding selenates.

$Mn_2P_2O_7$ .... = 3·5847 at 20°.
$Zn_2P_2O_7$ .... = 3·7538 at 23°.
$Ni_2P_2O_7$.................. = 3·9403 at 25°.
$Zn_2As_2O_7$ .... = 4·7034 at 21°.
$BeSO_4 4H_2O$.............. = 1·6743 at 22°.
$SnCl_2 2H_2O$ .... = 2·634 at 24°.
$HgCl_2(NH_4)_2Cr_2O_7H_2O$ .... = 3·2336 at 21°.
KIO_3.................... = 3·802 at 18°.
TeO_3.................... = 5·0704 at 14·5°.
$Mg_2P_2O_7$ .... = 2·5988 at 22°.
$Co_2P_2O_7$ .... = 3·746 at 23°.
$Mn_2As_2O_7$................ = 3·6832 at 23°.
$Mg_2As_2O_7$................ = 3·7305 at 15°.
$CrK_3C_6O_{12} 3H_2O$ .... = 2·1039 at 23°.
HgI_2CuI .... = 6·1602 at 15°.
$Hg(C_2H_3O_2)_2$ .... = 3·2544 at 22°.
TeO_2.................... = 5·7559 at 12·5°.
$BaTeO_4$.................. = 4·5486 at 10·5° (feebly ignited).

M. M. P. M.

Expansion of Liquids by Absorption of Gases. By J. J. MACKENZIE and E. L. NICHOLLS (*Ann. Phys. Chem.*, [2], iii, 134—142).—The method of determining the expansion by comparing the specific gravity of the liquid before and after the absorption, is condemned by the authors as being deficient in sensibility. Their own method consists in exactly filling a vessel with the liquid to be examined, which is then connected with a second vessel, and the gas to be absorbed is passed in, until the liquid is completely saturated. The portion which overflows into the second vessel from the expansion of the liquid is then weighed, as also that remaining in the first vessel.

The following table gives the average coefficients of expansion for water and carbonic anhydride determined in this way :—

Temperature.	Coefficient.	Temperature.	Coefficient.
2°	0·002144	17°	0·001240
6	0·001726	18	0·001280
8	0·001670	22	0·001210
12	0·001450	27	0·001190
14	0·001379	32	0·001010
16	0·001378		

On comparing these results with the coefficients of absorption, as given by Bunsen, it is seen that the expansion is directly proportional to the amount of gas absorbed. The density of the absorbed carbonic anhydride is found to approximate closely to the value given for the liquefied gas by Andrews (*Phil. Mag.* [5], I).

The expansion by heat of water saturated with carbonic anhydride was determined in a glass vessel having a narrow glass tube dipping into mercury. The vessel filled with the saturated aqueous solution of the gas was cooled about 2°, and the amount of mercury which passed into the narrow tube was determined. The following table was thus obtained:—

Temperature interval.	Average Temperature.	Coefficient.
4·0 — 1·90°	2·95°	0·0000604
5·8 — 3·40	4·6	0·0000610
7·4 — 4·80	6·1	0·0000679
12·15— 9·85	11·0	0·0000999
12·85—11·21	12·03	0·0001130
16·50—12·75	14·62	0·0001252
20·60—16·4	19·0	0·0001710
23·43—20·33	21·88	0·0001811
25·3 —23·46	22·88	0·0002170
27·55—25·0	26·27	0·0002526
29·15—26·32	27·73	0·0002923
31·7 —28·73	30·21	0·0002680

J. T.

Laws regulating Volume-changes in the formation of Alloys and in mixtures of Liquids. By K. Karmarsch (*Dingl. polyt. J.*, ccxxvi, 329—337, 441—455, 561—573).—The formation of alloys is generally accompanied by increase of volume, the mixing of liquids by diminution of volume.

In cases in which contraction alone occurs, if the results are arranged so that the amount of one ingredient gradually increases, a maximum point is reached, generally near the middle of the series; from this point the amount of contraction diminishes either way.

Where expansion alone occurs, the amount generally increases until a maximum point is reached, after which the amount of contraction diminishes, in some instances being equal to zero near the middle of the series: this result is not yet to be taken as universally applicable.

The amount of substance divided by percentage of volume-change gives a measure of the expanding or contracting force.

The results of experiments, original and otherwise, with a few alloys and with many mixed liquids are tabulated in great detail. For these details the original paper must be consulted. A few general results are here given.

Alcohol and Water.—As the amount of water increases, the contraction diminishes, until the change becomes one of expansion.

Sulphuric Acid and Water.—Contraction increases to a maximum point, 9·13 per cent., then diminishes, the rate of increase of diminution itself increasing. With mixtures of over 50 per cent. acid the contractile force of the water is greater than that of the acid; the contrary holds good for mixtures of less than 50 per cent. of acid.

Hydrochloric Acid and Water.—Contraction is small, and *increases* with *increase* of acid, until the maximum point is attained.

Nitric Acid and Water.—Contractile force is much less than in the case of sulphuric acid.

Acetic Acid and Water.—Generalisation made in cases of sulphuric and hydrochloric acid holds good here also. The contractile force is less than that observed with sulphuric acid, but greater than with nitric acid.

Ammonia and Water.—Contraction diminishes with increase of water until a point is reached, after which an irregular expansion is noticed, followed again by irregular contraction.

M. M. P. M.

Transpiration of Vapours. By L. MEYER (*Deut. Chem. Ges. Ber.*, xi, 206—211).—The author has devised an apparatus for experiments on the rate of transpiration of vapours. It is made entirely of glass, and consists of a flask in which the liquid under examination can be boiled at constant pressures, variable at pleasure within certain limits. In the neck of the flask is placed a capillary tube 0·3 mm. in internal diameter and more than a meter long, coiled into a spiral, of which one end terminates inside the neck, whilst the other end passes downwards and through the side of the flask (into which it is fused), and is connected with a condensing-arrangement of tubes exhausted of air, and so contrived that the volume of liquid condensed in them can be read off at intervals. The temperature of the condenser is kept constant by means of a stream of water, the temperature of which necessarily determines the pressure at that end of the capillary tube.

From the results of experiments on benzene made with this apparatus, the author concludes that the laws of transpiration of gases are not applicable without modification to saturated vapours. He has arrived, by purely empirical methods, at the following expression of the relation between the rate of transpiration and the pressure of saturated vapours.

The volume V, at pressure p, of a gas transpiring in the time t, is expressed by the equation—

$$V = C.\frac{t}{\eta}\frac{p_1^2-p_2^2}{p},$$

where C is a constant depending only on the dimensions of the capillary tube; p_1 and p_2 the pressures at the entrance and exit of the tube; and η the co-efficient of friction of the gas. Since $V.p$ represents the mass, Q, of the transpired gas—

$$Q = C.\frac{t}{\eta}(p_1^2-p_2^2),$$

that is to say, the quantities transpiring in equal times are, *cæteris paribus*, proportional to the difference of the squares of the pressures at the two ends of the capillary tube; and the times of transpiration of equal quantities are inversely proportional to this difference.

On applying this formula to the results of experiments with benzene, it is found that as p_1 increases, the product $t(p_1^2-p_2^2)$, for equal quantities Q, increases in the proportion of the square root of p_1; so that, for equal quantities transpired, $t.\frac{p_1^2-p_2^2}{\sqrt{p_1}}$ is constant, *i.e.*, it is independent of pressure (and therefore of temperature), and depends only upon the dimensions of the capillary tube and the nature of the vapour transpired. Hence, for one and the same apparatus, this quantity is a measure of the comparative rates of transpiration of different substances, and consequently of the dimensions of their particles. It follows, moreover, from the constancy of this quantity, that the coefficient of friction, η, of benzene-vapour (and probably of all saturated vapours) is proportional to the square root of the tension of the vapour.

Putting T for the time (in minutes) of transpiration of the molecular weight, M (in grams), $Q = M$ and $t = T$,

$$M = C.T.\frac{p_1^2-p_2^2}{\sqrt{p_1}}; \text{ and } T = \frac{M}{C}.\frac{\sqrt{p_1}}{p_1^2-p_2^2}.$$

In 27 experiments with benzene, in which p_1 varied from 760 to 699 mm., and p_2 varied from 210 to 51 mm.—

$$T.\frac{p_1^2-p_2^2}{\sqrt{p_1}} = 574 \text{ (mean).}$$

the greatest difference being less than 1 per cent. above or below this number.

A series of experiments with ethers of fatty acids is now in progress.

J. R.

Diffusion of Gases in Liquid, Viscous, and Solid Bodies. By S. v. Wroblewski (*Ann. Phys. Chem.* [2], ii, 481—513).—In diffusing through solid, viscous, or liquid bodies, gases, as a rule, obey a law similar to Biot and Fourier's law for the conduction of heat, viz., that the volumes of gas absorbed are proportional to the square roots of the times of absorption. In the author's experiments the gas usually employed was carbonic anhydride. He found that this gas did not diffuse through distilled water according to the above law, but with a much greater velocity than that law required, being in fact almost directly proportional to the time. If, however, any indifferent crystalloïd, such as sodium chloride, be dissolved in the water, the relation between the time and volume of gas absorbed changes according to the quantity of the solid dissolved, until after a certain concentration the rate of diffusion obeys Biot and Fourier's law. In the case of common salt this takes place when the liquid contains $\frac{1}{10}$th or more of its weight of dissolved salt. The same thing occurs if other crystalloïds, as sugar, &c., are used instead of sodium chloride.

This difference in behaviour of distilled water and water containing a sufficient quantity of dissolved substance is proved to be due solely to the influence of gravity. For distilled water saturated with carbonic anhydride has a greater density than pure water, and this is quite sufficient to explain why the gas does not diffuse through pure water according to Biot and Fourier's law; for the upper saturated, and therefore denser, layer of the water sinks to the bottom of the vessel, and so the circumstances under which pure diffusion takes place are completely obscured.

Carbonic anhydride likewise obeys Biot and Fourier's law in diffusing through glycerin, or concentrated solutions of glycerin in water, and also through colloïds, as gelatin and glue, dissolved in water.

The author concludes, therefore, that when a gas diffuses into a solid, liquid, or viscous body, it obeys the same laws as those which govern the propagation of heat through a solid rod, and that exceptions are to be ascribed to the action of gravity. T. C.

Inorganic Chemistry.

A Lecture-experiment. By IRA REMSEN (*Deut. Chem. Ges. Ber.*, xi, 234).—The author recommends the following arrangement for igniting hydrogen or water-gas in ascending soap-bubbles:—Some 5 or 6 feet above the middle of the lecture-table one of the largest glass funnels is suspended, mouth downwards, by means of wire. Beneath the centre of the funnel is a gas-burner, so arranged as to give a horizontal flame. Soap-bubbles liberated vertically below the funnel invariably come into contact with the flame. J. R.

Dissociation of Chlorine Hydrate. By M. ISAMBERT (*Compt. rend.*, lxxxvi, 481—484).—Chlorine unites with water at a temperature below 8° C., forming a solid hydrate which Faraday employed to obtain liquid chlorine. Repeating Faraday's experiment, it may be seen that the hydrate decomposes gradually at a temperature considerably above 8°, and on the other hand it will be found that, under certain circumstances, the hydrate still remains in a tube prepared for the liquefaction of chlorine, even in summer heat, one part being decomposed, another dissolved, and a third remaining intact. These observations led the author to examine by direct experiment the tension of the chlorine given off by the hydrate at different temperatures. He then gives a full description of the apparatus and method of conducting his experiments, and finds from his results that the tension of the chlorine gas given off by its hydrate is constant at the same temperature; thus two apparatus of different capacity containing different quantities of water and hydrate gave at 14·5° a tension of 1,400 mm., and at 11° with the same apparatus, tensions of 947 and 952 mm. The tension therefore M. Isambert considers as differing only with the temperature, and the phenomenon should be classed among those of dissociation discovered and studied by St. Claire Deville. To give an idea of the progress of the decomposition the author gives the following table:—

Temperature.	Tension.	Temperature.	Tension.
0·0°	230 mm.	8·8°	722 mm.
3·3	375 „	9·1	776
3·6	400 „	9·5	793 „
5·0	481 „	10·1	832 „
5·7	530 „	11·0	950 „
5·9	545 „	11·5	1015 „
6·6	571 „	11·7	1032 „
7·2	595 „	12·9	1245 „
7·6	644 „	14·5	1400 „
8·0	671 „		

These experiments explain the phenomena of the solubility of chlorine in water, namely, that below 9°, the hydrate alone is formed, which dissolves in the water; above this temperature and at ordinary pressures there is merely a solution of the gas in water; moreover, a current of air passing through a solution of chlorine below 9° is sufficient to carry off the gas, little by little, exactly as if there were solution and not combination. If a curve be traced representing the tensions of chlorine, it is found to resemble that of the tension of the dissociation of ammonium chloride. It approaches also that of ammoniacal silver chloride, $AgCl.3NH_3$, the pressures increasing a little more rapidly with the temperature.

J. M. T.

Stability of Ozone. By M. BERTHELOT (*Compt. rend.*, lxxxvi, 76).—The author uses flasks of about 260 c.c. capacity filled with oxygen ozonised by the discharge and kept at a temperature of about 12°.

At the commencement of the experiment, the gas contained 2·2 per cent. of ozone, in 24 hours the amount was reduced to 2·1 per cent., in 5 days to 1·5 per cent., in 14 days to 0·4 per cent.; after 51 days only a trace remained, and in 60 days no ozone could be detected either by the smell or by potassium iodide. The author observes that the rate of destruction of the ozone is directly proportional to the amount contained in the mixture, and that ozone has no fixed tension of dissociation; this is implied by its endothermic formation, in so far differing from the polymerides which disengage heat on their formation. These experiments were made on dry ozone; the presence of distilled water, however, did not appear to accelerate the dissociation, at all events in the first week.

The author remarks that ozone has been compared to a gas whose particles are charged with negative electricity, but he considers that this is not borne out by his experiments on the influence of the two electricities in its formation (*Ann. Chim. Phys.* [5], xii, p. 447), nor by the following experiment. Two flasks of the same capacity were taken, one of glass, which was isolated; the other of platinum, containing strips of the same metal and immersed in water. Both were filled with dry ozone; in 24 hours the ozone in the glass flask had diminished from 13 to 12, and that in the platinum 14 to 13; showing, he considers, that nothing had taken place analogous, in the ordinary sense, to a discharge of electricity. J. M. T.

Formation of Hydrogen Peroxide, Ozone, and Persulphuric Acid. By M. BERTHELOT (*Compt. rend.*, lxxxvi, 71—76).—The author discusses work done by former experimenters in this subject, and then details his own experiments, from which he draws the following results:—Ozone may be changed into hydrogen peroxide, if not directly, at all events by the intervention of ether, even when both are perfectly anhydrous, an intermediate compound being formed, viz., ozonised ether, which, by shaking with water, is converted into hydrogen peroxide. These two reactions are direct, disengaging a total of + 3·7 kilogram-degrees of heat for each unit of peroxide formed.

Hydrogen peroxide can be changed into persulphuric acid by means of concentrated sulphuric acid, care being taken that the temperature is not raised. This reaction takes place with the monohydrate, but not with the dihydrate of the acid, whence it may be inferred that the heat disengaged is less than that corresponding with the change of the one hydrate into the other, that is, less than + 1·5 kilogram-degrees.

Persulphuric acid in the cold slowly gives off all its oxygen in the ordinary state, which the author regards as characteristic of reactions taking place with disengagement of heat; there is therefore a successive loss of energy in passing from ozone through hydrogen peroxide and persulphuric acid to ordinary oxygen. The sum of energies lost in this series of transformations is 14·8 kilogram-degrees, which is equal to the amount absorbed in the production of ozone from oxygen by means of chemical or electrical energy. J. M. T.

Behaviour of Hydrogen Sulphide with Carbon Dioxide at a Red Heat. By H. KÖHLER (*Deut. Chem. Ges. Ber.*, xi, 205—206).—The author finds that when a mixture of equal volumes of these gases is passed through a glass tube heated to redness, the products of the reaction are water, carbon oxide, and free sulphur: $CO_2 + H_2S = H_2O + CO + S$. J. R.

Production of Ammonium Nitrite. By P. ZOELLER and E. A. GRETE (*Deut. Chem. Ges. Ber.*, xi, 2144).—The statements of Schönbein as to the oxidation of atmospheric nitrogen by ozone have been disproved by Bohlig, who found that the ammonium nitrite, said to be thus formed, pre-existed in the air, and by Carius and Berthelot who each found that moist nitrogen is not affected by ozone or by oxygen, neither nitrite nor nitrate being produced.

The authors find that when hydrogen is specially purified by passage through two permanganate wash-bottles, two potash tubes, and two pumice-stone sulphuric acid tubes, it does not affect Nessler's solution (which gives a precipitate with the crude hydrogen); when it is burnt in air purified in the same way, and hence freed from organic dust, &c., the condensed water always contains ammonium nitrite in minute quantities, but no appreciable amount of nitrate.

C. R. A. W.

On Schweitzer's "New Acid Ammonium Sulphates." By S. W. JOHNSON and R. H. CHITTENDEN (*Amer. J. of Sci.* [3], xv, 131—134).—The authors have carefully repeated the experiments of Schweitzer on the action of heat on ammonium sulphates. Their results show that at a temperature a little higher than the boiling point of mercury, ammonia and water are given off, whilst a mixture of the pyrosulphate with the normal and acid sulphate is left, thus:

$$6(NH_4)_2SO_4 = 5NH_3 + H_2O + 3NH_4HSO_4 + (NH_4)_2S_2O_7 + (NH_4)_2SO_4.$$

Near incipient redness, the reaction proceeds further, as represented in the following equation:—

$$3[NH_4HSO_4 + (NH_4)_2S_2O_7 + (NH_4)_2SO_4] = 2SO_3 + 2H_2O + 3NH_3 + 2NH_4HSO_4 + (NH_4)_2S_2O_7.$$

M. M. P. M.

Dissociation of Barium Carbonate. By M. ISAMBERT (*Compt. rend.*, lxxxvi, 332, 333).—The author has pointed out (*Revue des Cours Scientifiques*, 1876, No. 46) that the action of charcoal in the decomposition of barium carbonate, is to maintain around the carbonate an atmosphere in which the tension of carbonic dioxide is almost nothing, and thereby to enable the decomposition to continue. To prove this statement, barium carbonate was heated to about the melting point of copper in a current of an inert gas, such as nitrogen, when carbon dioxide was evolved. Barium carbonate is, therefore, decomposed in a manner similar to calcium carbonate.

L. T. O'S.

Solubility of Lime in Water. By A. LAMY (*Compt. rend.*, lxxxvi, 333—337).—The solubility of lime in water varies with its origin, its state of division, the temperature at which it has been prepared, its dehydration or recalcination at a red heat, the length of time it is left in contact with water, and, lastly, the continued heating of the milk of lime.

The least soluble variety of lime is that prepared from the carbonate precipitated from calcium nitrate by ammonium carbonate; whilst that prepared by the ignition of the crystalline hydrate, of marble, or of calcium nitrate, is the most soluble.

The crystalline hydrate dissolves very slowly in water at 30°. By washing the lime at a temperature of 30—40°, or by boiling the milk of lime for one or two hours, the solubility is temporarily diminished, but by recalcination its solubility is increased. Lime prepared from different sources, differs in solubility, but in a less marked degree at 100° than at lower temperatures. The author's results between 54° and 100° differ considerably from those obtained by Dalton and by Phillips. The hydrate which crystallises above 60° in flat regular prisms has the same formula, CaOHO, and the same sp. gr. 2·236, as that produced at the ordinary temperature. Vegetable fibre and paper absorb lime, so that the solution is very much weakened by filtration.

The author gives a table of the solubility of lime obtained from the nitrate, from marble, and from ignition of the hydrate, and has also mapped a curve, showing the variations in the solubility of lime with increase of temperature. L. T. O'S.

Extraction of Gallium. By LECOQ DE BOISBAUDRAN and E. JUNGFLEISCH (*Compt. rend.*, lxxxvi, 475—478).—The authors have operated, with the help of M. Thomas, upon 4,300 kilos. of zinc blende from Bensberg in the following manner:—

The pulverised blende having been roasted at a low temperature, whereby most of the indium is expelled, is treated with a sufficient quantity of sulphuric acid to convert the greater part of the zinc into sulphate, leaving a residue of subsulphate containing the gallium. This residue is redissolved in sulphuric acid, and after reduction of the iron by means of zinc, the filtrate is fractionally precipitated by carbonate of soda, the reaction being watched by means of the spectroscope. After a repetition of the operation last described, 100 kilos. of the moist material were obtained, which was sent to the laboratory for further treatment.

Here the operation of fractional precipitation was carefully repeated several times, and the sulphuric acid solution was evaporated until the greater portion of acid was expelled, and the solution then boiled with a large quantity of water. By this means titanic acid was eliminated. After purification with hydrosulphuric acid, acetate of ammonia was added to the liquid still containing a considerable quantity of zinc, and it was again treated with H_2S, whereby zinc sulphide was precipitated, carrying the gallium along with it, thus separating it from aluminium, which remains in solution. The addition of zinc sulphate and precipitation with H_2S is repeated as long as the sulphide gives gallium lines; the precipitate is dissolved in sulphuric acid, and the gallium thrown down by fractional precipitation with sodium carbonate, controlled by spectroscopic examination. After re-dissolution in the smallest possible quantity of sulphuric acid, the small quantities of Cd, Pb, In, and Zn remaining are removed by H_2S. The liquid is then again boiled with a large quantity of water and filtered hot, when a voluminous basic salt of gallium is obtained, which is washed thoroughly with boiling water. This salt is easily dissolved by solution of potassium hydrate, which leaves iron, indium, &c., undissolved. The alkaline liquid, on treatment with H_2S and the addition of dilute sulphuric acid, gives a deposit of sulphides, and the gallium is then again thrown down as subsalt, by diluting largely with water and boiling. The gallium is isolated by electrolysis from the potassic solution of the subsalt.

By this means 62 grams of metallic gallium were obtained, which, taking into consideration the loss and the small amount of the metal remaining in the materials treated, would give the amount of gallium in the blende of Bensberg at $\frac{1}{60000}$, or 16 mgrm. per kilo.

J. M. T.

The Solution of Molybdate of Ammonium in Nitric Acid. By S. KERN (*Chem. News*, xxxvii, 98).—In pure molybdic solutions, as ordinarily prepared for the precipitation of phosphoric acid, the yellowish-white precipitate, which usually deposits after several weeks, is a basic molybdic salt, and not a metameric form of molybdic acid, as stated by Jungck (*Zeitschr. Anal. Chem.*, xv, 52), who supposed it to be formed by the action of light. The precipitate is soluble in ammonia, and the quantity deposited depends upon the method followed in the preparation of the molybdic solution. Eggertz's method is the best.

A. J. C.

Sulphates of Vanadic Pentoxide. By B. W. GERLAND (*Deut. Chem. Ges. Ber.*, xi, 98—106).—Berzelius described two compounds, $V_2O_5.3SO_3$ and $V_2O_5.2SO_3$, formed by the action of sulphuric acid on vanadic acid. The author finds that vanadic acid dissolves in sulphuric acid in a manner varying with its preparation; the fused oxide dissolving more slowly than that prepared by the ignition of ammonium vanadate. $V_2O_5.3SO_3$ is prepared by dissolving vanadic oxide in excess of sulphuric acid at a low temperature; the excess of sulphuric acid is afterwards removed by heating in an air bath at 200°. The dry residue thus obtained is covered on the surface with a green compound, $V_2O_2.2SO_4$, which is insoluble in water, under which is the red crystalline compound, $V_2O_5.3SO_3$. This absorbs water from the air, forming a red syrup, which, on addition of water, is decomposed, vanadic acid separating out. The separation of the two abovenamed sulphates is effected by heating the mixture with dilute nitric acid, $V_2O_2.2SO_4$ remaining insoluble.

$V_2O_5.3SO_3$ is also formed by boiling V_2O_5 in sulphuric acid, separating out as ruby-red transparent octohedrons; but if the boiling be continued for some time, it comes out in golden-yellow needles. The simultaneous formation of $V_2O_2.2SO_4$, and the rapidity with which $V_2O_5.3SO_3$ absorbs moisture, render its preparation and analysis difficult.

Solutions of V_2O_5 in excess of sulphuric acid, heated for some time at 130—150°, yield an opaque red crystalline crust, which Fritsche regarded as $V_2O_5.H_2O.2SO_3$ (*Jahresb.*, 1851, 35); but which, according to the author, is impure $V_2O_52SO_3$.

The basic sulphate, $V_2O_5.2SO_3$, is obtained by heating the neutral salt ($V_2O_5.3SO_3$) at the temperature of melting lead, until sulphuric anhydride ceases to be expelled. Thus prepared, the basic sulphate is a red crystalline mass, deliquescing in moist air to a brown solution, which, on dilution with water, yields a precipitate of vanadic oxide.

Dialysis of Sulphuric Acid, Solution of Vanadic Acid.—(1.) A solution of V_2O_5 in hot sulphuric acid, was diluted with water, and dialysed into water. At first sulphuric acid diffuses out rapidly, and a solution is left in the dialyser, containing vanadic acid and sulphuric acid in the proportion of 3 molecules of the former to 1 molecule of the latter. If the diffusion be continued for some time, the dialysed product contains vanadic acid and sulphuric acid in the proportion of 2 molecules to 1 molecule.

(2.) A solution of V_2O_5 (prepared by igniting ammonium vanadate) in cold sulphuric acid was dialysed into water: the sulphuric acid diffuses out, and vanadic acid separates in the dialyser, whilst the liquid contains sulphuric and vanadic acids in the proportion of 1 molecule to 1·32 molecule. This difference in the two cases, the author attributes to the cold solution containing only a molecular compound of V_2O_5 and H_2SO_4; whilst the solution prepared by the aid of heat contains the atomic compound $V_2O_2.3SO_4$, which is the neutral salt of vanadylic oxide, $V_2O_2.O_3$, whilst $V_2O_2.O.2SO_4$ is the basic salt.

Double Salts of Vanadylid Sulphates.—Calculated quantities of $V_2O_33SO_4$ and K_2SO_4 dissolved in water and mixed, yield on heating to a blood heat amber-coloured crystals, in transparent or turbid nodules. The crystals have the composition $K_2O.V_2O_5.2SO_3 + 6H_2O$, and are decomposed by water with liberation of vanadic acid as a brown mud, containing some potassium. The author considers that in these compounds the potassium enters into combination with the vanadyl, and that the rational formula of such a compound is $V_2O_2(OK)_2(O_2SO_2)_2$. All attempts to form an alum have failed.

Ammonium sulphate forms a double salt similar to the potassium double salt, having the composition $V_2O_2(ONH_4)_22SO_4 + 4H_2O$. It crystallises in nodular masses, which are formed of needles grouped together, and it dissolves in water without separation of vanadic acid.

Sulphates of sodium and magnesium yield no double salts.

P. P. B.

Cast Nickel: combining of Carbon and Silicon with Nickel. By W. E. GARD (*Am. J. of Sci.* [3], xv, 274—277).—Analyses of cast nickel are detailed, showing from 0·4 to 1·9 per cent. of carbon, and from 0·12 to 0·3 per cent. of silicon.

By reducing a mixture of nickel oxide and powdered quartz by means of charcoal, a white button was obtained, which contained from 9 to 9·5 per cent. of carbon and 6·19 per cent. of silicon; the specific gravity of this substance was 7·73. By fusing commercial nickel with charcoal, a product resembling grey pig-iron was found of sp. gr. 8·04, containing total carbon, 2·12; graphitic carbon, 2·03; silicon, 0·36.

Nickel in thin plates (1), the same prepared by reduction of the oxide in hydrogen (2), fine soft iron wire (3), and cobalt prepared by ignition of pure oxalate and reduction in hydrogen (4), when severally heated to redness in a stream of marsh gas, gained the following amounts of carbon:—

(1.)	(2.)	(3.)	(4.)
10·649	5·96	0·795	12·758 per cent.

Experiment showed that the carbon had entered into combination with the metal.

M. M. P. M.

Iodates of Cobalt and Nickel. By F. W. CLARKE (*Am. J. of Sci.* [3], xv, 280—285).—By dissolving cobalt carbonate in aqueous iodic acid and evaporating rapidly, Rammelsberg's iodate $CoI_2O_6.1\frac{1}{2}H_2O$ separates out, but if the solution be allowed to evaporate spontaneously, normal cobalt iodate, $CoI_2O_6.6H_2O$, separates in small red crystals, which lose 4 molecules of water at 135°; the remaining water cannot be expelled without decomposing the salt. Sp. gr. of the crystals = 3·6426 at 16° and 3·6893 at 21°. Nickel iodate, $NiI_2O_6.6H_2O$, forms small green crystals; it is prepared in a manner similar to that described for the corresponding cobalt salt. Sp. gr. = 3·6954 at 22°.

M. M. P. M.

Absorption of Hydrogen by Copper Spirals. By O. LIETZENMAYER (*Deut. Chem. Ges. Ber.*, xi, 306—309).—The hydrogen absorbed by a freshly-reduced spiral of copper-wire gauze, as used in organic analysis, is not expelled at 160°. When such a spiral is heated in a tube closed at one end, its surface oxidises at a temperature between 200 and 250°, but at a dull red heat water is formed, and reduction again takes place. From 0·5 to 0·6 mgm. of water were obtained for every gram of copper heated. The occluded hydrogen may be removed by heating the spirals at 250° until they become slightly oxidised on the surface, and then heating them to redness in a nearly closed tube, when they regain their metallic lustre.

W. C. W.

Colour Relations of Copper and its Salts. By T. BAYLEY (*Phil. Mag.* [5], v, 222—224).—The colour transmitted by dilute solutions of copper sulphate is shown to be complementary to that reflected by the metal. The author hopes to found upon this fact a method for the estimation of copper in dilute solutions.

M. M. P. M.

Presence of Oxygen in Metallic Silver. By J. DUMAS (*Compt. rend.*, lxxxvi, 65—71).—The experiments described in this paper arose out of a discussion lately carried on in the "Academie des Sciences" on the subject of the atomic theory.

The author commences his paper by saying that a certain number of compounds, of which chloral hydrate is one, give 4 volumes of vapour on becoming gaseous; and he then asks whether the excess of density of certain vapours, such as acetic acid, or sulphur near its boiling point, is due to a rapid change in the coefficient of dilatation, or to a polymeric condensation of the molecules of the body which would make sulphur at 500° the allotropic variety of that body. He considers that the solution of these questions may now be left in the hands of the able experimenters engaged in this branch of research. A third question, however, of great importance in the conception of the constitution of matter still remains undecided—namely, whether the equivalents are really simple ratios of the equivalent of hydrogen taken as unity. This theory has lately again been called in question, but the author believes that the discrepancies, both in the practical carrying out of the theory, and those found in the determinations of various experimenters, may be ascribed to errors of calculation, and, above all, to impurities in the bodies employed. Thus all the determinations of the densities of gases, as compared with hydrogen at the beginning of the century, differed slightly from the whole numbers required by theory, this being due, as the author shows, to the fact that the details of manipulation at that time were not sufficiently accurate. He then enumerates conditions which he considers indispensable for accurate experiments relating to this branch of research, such as weighing in a vacuum, the use of pure substances, the simplest possible reactions, and the keeping of the body in a vacuum at a high temperature until all evolution of gas has ceased, giving, as an example, silver chloride. This body is one of the most useful in the determination of equivalents, as the relation between chlorine and silver is so easily determined, and the insolubility of silver chloride allows all soluble chlorides to be determined with great precision. Still, however, on comparing the results of different experimenters on the synthesis of silver chloride, great differences are found: thus, for 100,000 of silver—

Berzelius found	132,700 AgCl.
Marignac found	132,842 „
Stas found	132,850 „
Dumas found	132,870 „
Gay-Lussac found	132,890 „
H. Rose found	133,014 „

There can be no question as to the competence of the above experimenters, and therefore the divergence must be looked for in the circumstances of the experiment.

These considerations have led the author to repeat the experiment at the *Ecole Centrale*, and they have since been repeated at the *Ecole Normale*.

For his experiments, a kilo. of pure silver was prepared by M. Debray by fusion with borax and nitre in the usual manner. This silver was placed in a flask of glazed porcelain and connected with a Sprengel pump. On heating the flask to 500°, gas began to be evolved; this continued for six hours, and the gas was collected in test tubes over mercury. When the evolution of gas completely ceased, the temperature was raised to the melting point of silver, but no further evolution took place. After cooling, the silver was found in a well-crystallised mass, which, after careful cleaning, showed a density of 10·512, being slightly above that generally attributed to pure silver. The gas disengaged was pure oxygen, 1 kilo. of silver giving at 0° and 760 mm., 57 c.c.; thus, 1 kilo. of silver contained 999·918 grams of silver and 82 mgrm. of oxygen. Another kilo. of silver, kept fused for 15 minutes, and into which were thrown small quantities of nitre, subsequently gave 158 c.c. of gas at 0° and 760 mm., weighing 226 mgrm.; therefore, the real weight of silver in the kilo. was only 999·774 grams. A third kilo. of silver, prepared by fusing the chloride with sodic carbonate and nitre, gave 174 c.c. oxygen, equal to 249 mgrm. From these results it is easily seen that in former experiments, where silver has been employed for determining chemical equivalents, it must have contained from 50 to 200 c.c. of oxygen per kilo. The author draws attention to the fact, that, on making the correction for this absorption of gas, the results of Marignac, Stas, and

Berzelius are brought into accordance with theory. In conclusion, he points out that when silver is maintained for some time at a low red heat in a vacuum, all trace of oxygen is extracted; if now the silver be fused and oxygen introduced, it is rapidly absorbed, even at the temperature at which porcelain becomes softened. He therefore considers that the tension of solution of oxygen in silver or the tension of dissociation of the compound (if it be considered one), may be determined. On cooling, the silver solidifies, disengaging the oxygen with considerable violence; but although this action is intensified in a vacuum, the silver does not even then lose the whole of the oxygen.

He considers these experiments to show that silver containing oxygen does not lose it in the cold in a vacuum; but that between 400° and 600°, it is disengaged, and under the same conditions, whilst at cherry-red heat the evolution of gas somewhat ceases. On the other hand, the phenomenon is reversed when the silver becomes pasty, and still more so when it is fused; moreover, on solidifying, although the metal loses some oxygen, it still retains a considerable quantity.

J. M. T.

Solubility of Silver Salts. By J. M. Eder (*J. pr. Chem.* [2], xvii, 44—47).—Solubility in alcohol. 100 pts. of spirits of wine containing—

Percentage of alcohol vol.	95	80	70	60	50	40	30	20	10
Dissolve at 15° of silver nitrate..	3·8	10·3	22·1	30·5	35·8	56·4	73·7	107	158
„ 70°	7·3	—	—	58·1	—	98·3	—	214	—
„ 75°	18·3	42·0	—	89·0	—	160	—	340	—

The author made another series of experiments by ascertaining how many grams of silver nitrate were contained in 100 c.c. of saturated solution of alcohol at different temperatures and of different strengths:—

Percentage of alcohol vol.	95	80	70	60	50	40	30	20	10
At 15° contained	3·0	8·6	21·0	27·1	33·4	52·8	60·6	89·1	130
„ 75 „	12·5	33·6	—	51·0	—	108	—	—	—

Ether dissolves only traces of silver nitrate.

100 pts. of a mixture of 1 vol. of alcohol (95 p.c.) with 1 vol. of ether, dissolved at 15°, 1·6 pts. of silver nitrate.

100 pts. of a mixture of 2 vols. of alcohol and 1 vol. of ether, dissolved 2·3 pts. of silver nitrate.

100 pts. of water saturated with ether dissolved 88·4 pts. of silver nitrate, at 15°.

100 pts. of water at 18° dissolved 0·58 pts. of a silver sulphate.

At 18°, 100 pts. of water, containing 5 and 15 per cent. of ammonia sulphate, dissolved respectively 0·66 and 0·85 pts. of silver nitrate.

At 18°, 100 pts. of water containing 12 and 37 per cent. of crystallised sodium sulphate, dissolved 0·65 and 0·80 pts. of silver nitrate.

At 18°, 100 pts. of water, with 6 and 8 per cent. of potassium sulphate, dissolved respectively 0·60 and 0·76 pts. of silver nitrate. This shows that alkaline sulphates do not affect the solubility of silver sulphate. S.

Mineralogical Chemistry.

Certain Volatile Products from Burning Coal-mines. By M. Mayençon (*Compt. rend.*, lxxxvi, 491—493).—In certain districts in the coal basin of the Loire, it is often observed that in the rubbish of pits in working there occurs at many points fumes or flames visible more especially at night. The same phenomena appear in certain burning mines, abandoned in consequence of their having taken fire. Around these fumerolles white, red, orange, yellow, and black incrustations occur, accompanied by a thick and hard crust. The author has studied the products composing these incrustations, which result from the action of the adjacent fire and the air on the elements of the coal and the neighbouring schist. He gives the following list of the substances found:—

I. *Efflorescence.*—*a.* White.—Ammonium chloride, bromide, and iodide; arsenious acid; aluminium and a little glucinum, probably chlorides.

b. Red.—Realgar melted and crystallised in oblique prisms.

c. Orange.—Ammonium chloride, bromide, and iodide; aluminium and glucinum chlorides, or sulphates; amorphous realgar, orpiment; octahedral sulphur.

d. Yellow.—Same products as last, except realgar.

e. Black.—Arsenic; ammonium arsenite; ammonium sulpharsenates and sulphates; sulphites and hyposulphites.

II. *Crust.*—Ammonia and potash alums; aluminium sulphate (large quantities); sulphates of iron; ammonium sulphate, chloride, bromide, and iodide. Arsenical compounds. Crystallised arsenic. Galena sublimed in cubes. J. M. T.

Pyritous Silver Ores. By A. Weisbach (*Jahrb. f. Min.*, 1877, 906—913).—*Argyro-pyrites.*—In the collection of Bergmeister Perl, at Marienberg, in Saxony, the author found various specimens of silver-ore, which had been obtained from the rich newly discovered lode in the Rudolf-shaft, at Marienberg. One specimen, which was crystallised, had a bronze-yellow colour on freshly broken surfaces; it was brittle, dense, and hard as fluorspar. The crystals have a hexagonal type, and exhibit apparently the combination $\infty P.P$, also $\infty P2$ secondary. The prism ∞P is often striated vertically, and occasionally feather-like; but on some specimens it is also perfectly smooth. The pyramid P striated parallel to its combination-edge with ∞P, and its edges are ften rounded off, so that there appears to be only one convex-globular or cupola-like face terminating the crystal. No distinct cleavage direction was apparent. Streak, deep black. Sp. gr. 4·06—4·12. A steel-blue tarnish is often observed upon the crystals. A specimen of the same mineral, found shortly afterwards in the Himmelsfürst Mine, was analysed, and found to have the following composition, viz.:—

Ag.	Fe.	S.
29·75	36·28	32·81 = 98·84

From this analysis it is evident that the mineral occupies an intermediate position between sternbergite and argento-pyrites, as will be apparent from the following analyses:—

		Ag.	Fe.	S.		
Sternbergite	1.	32·0	36·0	30 =	99·2	(Zippe).
,,	2.	35·27	35·97	29·10 =	100·34	(Rammelsberg).
Argento-pyrites	3.	26·50	39·30			

The general formula, $Ag_3Fe_{6+n}\ S_{9+2n}$, can be used for the three minerals above mentioned, the full formulæ being as follows, viz.:—

For sternbergite.. = $Ag_3Fe_6S_9$ (Joachimsthal).
,, argyropyrites = $Ag_3Fe_7S_{11}$ (Freiberg, Himmelsfürst).
,, argentopyrites = $Ag_3Fe_9S_{15}$ (Joachimsthal).

Argyropyrites differs in its physical properties from (1) sternbergite, in crystal type and greater hardness; (2) argento-pyrites, in being softer and less brittle than that mineral. Crystals of argyropyrites are often grouped into hemispherical masses, resting upon pearl-spar, and are always accompanied by arsenical red silver-ore (pyrargyrite). Schrauf (*Berichte der Wiener Akademie*, 1871) is of opinion that argyropyrites is a rhombic mineral, the obtuser prismatic edge measuring 119° 40′, and the lateral edge of the pyramid, 57° 0′; and the author agrees with him. One crystal from Marienberg, which closely resembled the combination $\infty P.0P$ in the hexagonal system, exhibited a horizontal striation on two of the vertical faces (the brachypinacoïd), the other four being partially smooth, or else showing a feather-like striation (the two systems of striæ intersecting each other almost at right angles). A very obtuse macrodome, the prism $\infty\breve{P}12$, and a secondary pyramid were also observed, with evidence of a twin or triplet formation. Freiberg argyropyrites is distinguished from that of Marienberg by the greater size and more complete development of its crystals, and also by its distinct basal cleavage. The author observed some pyramidal crystals of argento-pyrites from the Neu Leipziger Grube, at Johanngeorgenstadt, resting upon thin tabular sternbergite, from which it may be inferred that the three related minerals described above can pass over from one into the other. Weisbach also mentions the discovery of a magnificent transparent specimen of pyrargyrite, in the "Beschert Glück Grube," at Freiberg, 35 mm. in length, and 28 mm. in width, exhibiting the following forms in combination, viz.:—$R_3.\infty P2.R.-\frac{1}{2}R.R_5$, and traces of $\frac{1}{4}R.\frac{1}{4}R_3.R_2$. This splendid crystal is now in the mineral collection at Freiberg.

C. A. B.

Crystallographical and Optical Examinations of Glauberite. By H. LASPEYRES (*Jahrb. f. Min.*, 1877, 947—948).—The glauberite crystals from Aranjuez are not so large as those from Ciempozuelos, near Villarubia (never being more than 20 mm. in length), but are characterised by complete absence of colour, stability in air, and development. The general combination observed is $-P.\infty P.0P.\infty$₽∞, and secondary, 3₽ and P. The measurements of the fundamental angles obtained by the author approach very closely those obtained by v. Zepharovich (*Jahrb. f. Min.*, 1874, 543), on the glauberite of Westeregeln. $C = 67° 49' 33''$, and $a : b : c = 1·220924 : 1 : 1·0270307$. The glauberite of Aranjuez is found on nodules of grey clay. The author concludes from an optical examination of this and a few other minerals, that all optical properties are independent of the chemical constitution and crystallographical system (minerals crystallising in the rhombic system being exceptions), and the same law applies to all diaxial media, irrespective of temperature. C. A. B.

Szmikite, a New Manganous Sulphate. By T. VON SCHROECKINGER (*Jahrb. f. Min.*, 1877, 729).—This mineral is amorphous, and forms stalactitic masses, with a mammellated surface. Fracture uneven. H = 1·5. G = 3·15. Colour, dirty white; freshly broken surfaces reddish-white. If a few fragments are left for a few days in a damp place, the fresh surfaces acquire a deep red colour, and there is a slight increase in weight. Analyses:—

	SO_3.	MnO.	H_2O.
I	47·43	41·78	10·92
II	47·11	41·61	11·19

The formula is therefore $MnSO_4 + H_2O$. Locality, an abandoned mine at Felsöbanya. G. T. A.

An Analysis of Siberian Volborthite. By F. A. GENTH (*Jahrb. f. Min.*, 950—951).—Occurs as a crystalline incrustation on quartz, at Woskressenskoi, in the Government of Perm. Colour, siskin to yellowish-green, with a pearly lustre. Chem. comp.:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CuO.	CaO.
1.......	1·38	4·45	1·77	3·01	34·04	4·29
2.......	1·36	4·78	0·45	1·42	38·01	4·49

	BaO.	V_2O_5.	H_2O.
1.	4·29	13·62	33·15 = 100·00
2.	4·30	13·59	31·60 = 100·00

The author considers the silica, alumina, ferric oxide, magnesia, and a portion of the water to be impurities, and the volborthite of Woskressenskoi to be a combination of barium, calcium, and copper vanadates, with cupric hydrate and water of crystallisation, the formula being $(\frac{1}{8}Ba\frac{3}{8}Ca\frac{4}{8}Cu)_3V_2O_8 + 3CuH_2O_2 + 12H_2O$. C. A. B.

Leadhillite from Matlock. By EM. BERTRAND (*Compt. rend.*, lxxxvi, 348—350).—This mineral appears to be crystallographically identical with the leadhillites already known. It was not analysed.

The separation of the axes in air for yellow light is $2E = 72°$, whilst the leadhillites of Scotland and Sardinia gives $2E = 21°$. The effect of heat on the separation of the axes is different. In the leadhillite of Scotland the axes gradually approach each other, and coincide at a temperature of 150°, beyond which the mineral becomes opaque; the Matlock specimen can be heated to 250°, without becoming opaque, and the axes are still 66° apart. J. T.

Coloradoite, a New Mineral. By F. A. Genth (*Jahrb. f. Min.*, 1877, 949—950).—Occurs disseminated in granular masses. Cleavage not distinct; fracture uneven. H = 3. Sp. gr. 8·627. Iron-black to grey, metallic lustre, often with a variegated tarnish. Decrepitates in the matrass, furnishing a sublimate of mercury. Heated on charcoal before the blowpipe it colours the flame green, and gives a white deposit. Soluble in nitric acid. Chem. comp. = Hg 60·89, Te 39·02 = 99·91, whence the formula HgTe is obtained. Coloradoite is found in the Keystone and Mount Lion Mine, accompanied by tellurium and quartz; in the Smuggler Mine it is accompanied by tellurium and gold. C. A. B.

Calaverite. By F. A. Genth (*Jahrb. f. Min.*, 1877, 950).—Was described by the author in the *Jahrb. f. Min.*, 1868, 845, but he obtained a further supply from the Keystone and Mount Lion Mine, and found its chemical composition corresponded with the formula, $(\frac{7}{8}Au\frac{1}{8}Ag)Te_2$. It occurs in fine streaks or granular masses in the above-mentioned mines, the crystals of this mineral being indistinct, and the crystallographical system undeterminable. Probably calaverite is the same mineral as Kreuner's bunsenine and vom Rath's kreunerite (*Jahrb. f. Min.*, 1877, 825). C. A. B.

Sylvenite from Grand View Mine, Colorado. By F. W. Clarke (*Am. J. of Sci.* [3], xv, 286).—An analysis of this mineral gave the following numbers:—

Te.	Au.	Ag.	Te.	S.
52·96	26·39	10·55	4·45	5·62 = 99·97

Eliminating pyrites, the analysis becomes—

Te.	Au.	Ag.
58·91	29·35	11·74 = 100·00

M. M. P. M.

Native Tellurium in Colorado. By F. A. Genth (*Jahrb. f. Min.*, 1877, 951).—Occurs at the Kensington Mine and Mount Lion Mine, Boulder County, crystallised and crystalline. Crystals small and distorted, occasionally strongly striated prismatic faces, rhombohedra, and the basal terminal plane are observed. Tellurium is also found at the above-mentioned localities disseminated, and in thin laminæ between other minerals. In the Smuggler Mine, small, brilliant crystals of tellurium are found, exhibiting the combination $\infty P.P.$, the prism being strongly striated. At a greater depth in the mine it occurs granular, accompanied by sylvanite. Chem. comp. as follows, viz.:—

Te.	Au.	Ag.	Hg.	Cu.	Pb.	Fe.	MgO.
99·94	3·40	1·69	1·07	0·51	0·74	0·12	0·12 = 107·47 (?).

At John Jay Mine, in the Central District, Boulder County, granular masses of tellurium are sometimes found 25 lbs. in weight. Colour, tin-white to lead-grey. Chem. comp. as follows, viz.: —

Au.	Ag.	Zn.	Fe.	Te.
1·04	0·20	0·32	0·89	97·94 = 100·39

C. A. B.

Sipylite, a New Niobate from Amherst County, Virginia. By J. W. MALLET (*Am. Jour. of Sci.* [3], xv, 397—402).—The new mineral is associated with albanite and magnetite, and occasionally a few large crystals of hydrous zircon. It appears in little irregularly-shaped masses, very brittle, exhibiting small, but distinct, conchoïdal and also uneven fracture. Colour, brownish-black; in thin splinters, red-brown; streak, light cinnamon-brown; lustre, resinous and pseudo-metallic; translucent in thin splinters; hardness = nearly 6; specific gravity, 4·89. When heated before the blowpipe the mineral decrepitates, and glows brilliantly, becoming pale greenish-yellow and opaque. The following are the analytical results:—

$Nb_2O_3Ta_2O_3$.*	WO_3.	SnO_2.	ZrO_2.	Eb_2O_3,Y_2O_3.†	Ce_2O_3.
48·66	0·16	0·08	2·09	27·94	1·37

La_2O_3.	$Di_2.O_3$.	WO.	MnO.	FeO.	BeO.	MgO.
3·92	4·06	3·47	trace	2·04	0·62	0·05

CaO.	Li_2O.	Na_2O.	K_2O.	F.	H_2O.
2·61	trace	0·16	0·06	trace	3·19 = 100·48

Grouping together the acid oxides of Nb, Ta, W, Sn, and Zr, reducing all the basic oxides present to the equivalent amounts of dyad oxides, and leaving out the water, the formula $R_3''M_2^{v}O_8.4R_2''M_2^{v}O_7$ is obtained.

If the water be included, and considered basic, the formula is that of an ortho-niobate, $R_3''M_2^{v}O_8$. The author is inclined to favour this method of regarding the new mineral. M. M. P. M.

Sonomaite, a New Mineral. By HAYDEN (*Jahrb. f. Min.*, 1877, 941).—Is crystalline. Sp. gr. 1·604. Colourless, with a silky lustre. Chemical composition as follows, viz.:—

Al_2O_3.	FeO.	MgO.	SO_3.	H_2O.
8·36	1·56	7·51	38·30	44·27 = 100·00

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* Ta_2O_3 = about 2 per cent.

† Y_2O_3 = about 1 per cent.

The formula corresponding with the chemical composition is $Al_2S_3O_{12} + 3MgSO_4 + 33H_2O$, therefore sonomaite belongs to the alum-group, and approaches most nearly to magnesia-alum. Sonomaite is found in the neighbourhood of the geysers in Sonoma County, California.

C. A. B.

On the Phosphorite Beds of Estremadura. By O. WOLFENSTEIN (*Landw. Versuchs.-Stat.*, xxi, 245—258).—The materials for this paper are taken from the report of the Geological Survey of Spain. After describing the geographical position and geological surroundings of the phosphorite beds, the author gives a series of tables of analyses of the different varieties of phosphorite occurring therein. These varieties are classified as follows:—1. Apatite in crystals. 2. Crystalline apatite. 3. Fibrous phosphorite. 4. Scaly or lamellar phosphorite. 5. Dense phosphorite. 6. Earthy phosphorite. The chief constituent of all the varieties is tricalcic phosphate, the proportion of which varies from 94 per cent. in the first, to 71·5 per cent. in the last. Other constituents are calcium fluoride and carbonate and silica in greatly varying proportions, together with small quantities of alumina, ferric oxide, and manganese dioxide.

All the phosphorite beds at present known have been discovered at intervals during the last twenty years, with the exception of one, which was discovered about the end of last century. In most cases the discovery of a new bed has led to the commencement of mining operations, generally by English capitalists; but, owing partly to faulty methods of working, partly to disputes about mining rights, and more especially to the great cost of transport of the mineral, the sanguine hopes entertained at first have not been realised. The result is that most of the older workings have now been abandoned. The average value of the phosphorite at the mines is estimated to be about twelve shillings per ton, whilst the cost of conveying it to England, whither it is almost exclusively sent, amounts to four times that sum. In dry seasons, when water-carriage fails, the mineral has to be carried long distances on the backs of animals. It has been proposed to facilitate transport by the construction of railways and other means, but hitherto nothing has been done. Some idea of the importance of these phosphorite beds may be gathered from the fact that one of them alone is estimated to contain at least 1,300,000 tons, and another 397,000 tons of the mineral.

J. R.

Leucite. By H. BAUMHAUER (*Jahrb. f. Min.*, 1877, 646).—The author finds that (1) the quadratic pyramidal surfaces of leucite differs from the biquadratic in being less soluble; (2.) The twinning of both outcast and enclosed leucite follows the law of G. vom Rath. (3.) The varying angular values are explained by the repeated symmetrical or unsymmetrical twinning. (4.) There are no real grounds for assigning the enclosed crystals to any other than the quadratic system.

G. T. A.

Dysanalyte, a Mineral resembling Pyrochlore. By A. KNOP (*Jahrb. f. Min.*, 1877, 647).—This mineral has hitherto been known as perowskite. According to Knop's analysis it consists of—

TiO_3.	Nb_2O_6.	CeO. Ce_2O_3.	CaO.	FeO.	MnO.	Na_2O.
41·47	23·23	5·72	19·77	5·81	0·43	3·57

The mineral is hexahedral. Sp. gr. = 4·13. It occurs at Vogtsburg in the Kaiserstuhl. G. T. A.

Gismondine. By A. Schrauf (*Jahrb. f. Min.*, 1877, 944).—The author confirms the statement of Seligmann (*Zeitsch. f. Kryst.*, 1877, iv, 336), that the gismondine of Salesl in Bohemia is rhombic, the crystals exhibiting a combination of the prisms with a brachydome and a macrodome. He found the type to be quadratic and the crystals to resemble closely those of bournonite. The axial relations were $a : b : c = 0·99246 : 1 : 0·94897$. An interesting observation was made on the succession of the zeolites in the druses of Salesl, it being evident that analcime was the oldest formation, natrolite the next in succession, and gismondine the last. Gismondine very often occurs in the place of apophyllite, the latter mineral being a younger formation than natrolite. The succession of the zeolites depends upon the degrees of solubility of their several constituents, the more recent formations being the most insoluble. C. A. B.

Garnet in a Cambrian Clay-slate from Lemmingstorp, Kirchspiel, Motala, Ostgotland. By E. Svedmark (*Jahrb. f. Min.*, 1877, 731).—The mass of the slate consists of a greyish aggregate of very fine particles, which can only partly be resolved by the microscope, and contains no visible cementing material. Amongst the imbedded minerals were recognised numerous often indented quartz grains, talc or mica, yellow to brownish ochreous particles, bluish-green generally semi-amorphous crystals of tourmaline, acicular bright green crystals, probably hornblende, and garnet in abundance. The slender needles so characteristic of the clay-slates, especially the older ones, were almost wanting, as is the case in specimens from other Swedish localities. The garnet occurs in regular crystalline layers, and in grains which, when small, sometimes contain a dark nucleus. Small crystals also occur, either isolated or in groups, in the laminæ of the talc. The author supposes that the garnet has not been formed simultaneously with the other constituents of the slate, but at a later period, while, however, the mass was still plastic. G. T. A.

Occurrence of Garnet in the Trap-rocks of New Haven, Connecticut. By E. Dana (*Jahrb. f. Min.*, 1877, 948—949).—These so-called trap-rocks belong to a group of eruptive masses which occur in the mesozoic sandstone district; they consist of felspathic basalt and olivine-diabase. At East Rock, garnet is found on the vertical faces of the rocks, generally clothing their surfaces in rosette-like crystalline aggregations, accompanied by magnetite, apatite, augite, and calcite. Distinct crystals (exhibiting the combination $\infty O . 2O2$) are rare at East Rock. Colour, dark-brown, yellowish-brown to black. Strong vitreous lustre. Sp. gr. 3·740. Chemical analysis shows that the garnet of this locality is the variety called melanite, as will be apparent from the following, viz.:—

SiO_2.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	Loss.
35·09	29·15	2·49	0·36	32·80	0·24	0·35 = 100·48

The author did not detect the presence of titanic acid in the above-mentioned garnets, but observed that apparently pure melanite crystals were often penetrated by acicular apatite. At Mill Rock, garnets are found at the point of contact between trap and sandstone, and are, no doubt, a secondary product of the decomposition of the former rock. The finest crystals at the latter locality are found in lines in the trap, or else filling hollow spaces in it and attached to quartz. These crystals appear at first sight to be the form ∞O, but a closer examination proves them to be a combination of a very obtuse hexakis-octohedron $64O\frac{64}{63}$ with $2O2$, $\frac{7}{2}O\frac{7}{2}$ and $\infty O \infty$ (the latter very subordinate). The hexakis-octohedron has been observed up to the present time, only on the topazolite of Piemont, whilst the form $\frac{7}{2}O\frac{7}{2}$ is new to garnet. Mill Rock garnet has a wine-yellow colour and a strong vitreous lustre. C. A. B.

Polluxite and Petalite from Elba. By C. RAMMELSBERG (*Deut. Chem. Ges. Ber.*, xi, 194—195).—An analysis of polluxite, of sp. gr. 2·868, gave the following numbers:—

SiO_2.	Al_2O_3.	Cs_2O.	K_2O.	Na_2O.	H_2O.
48·15	16·31	30·00	0·47	2·48	2·59 = 100,

from which the author deduces the formula—

$$R_2AlSi_5O_{14} + Aq. = R_2Si_2O_5,3R_2SiO_3 + Aq.,$$

or, assuming the water to be chemically combined,

$$R_4AlSi_5O_{15} = 2R_2SiO_3,AlSi_3O_9.$$

Petalite, of sp. gr. 2·386, gave on analysis—

SiO_2.	Al_2O_3.	Li_2O.	Na_2O.	K_2O.	Loss.
78·07	17·35	2·77	1·04	0·43	0·34 = 100

These two minerals resemble each other so closely that, independently of their chemical behaviour, they are distinguishable only by their specific gravity and optical characters. J. R.

Appearance of Gadolinite, Orthite, and similar Minerals under the Microscope. By A. SJÖGREN (*Jahrb. f. Min.*, 1877, 730—731).—The author finds that the gadolinites of Falun, Ytterby and Hofers, the orthites of Stockholm, Ytterby, Sandö, Ödegaard and Helle, are isotropic, whilst thin sections from eleven different localities were either partly or entirely double-refracting. Of the isotropic varieties the Swedish are greenish and paler by transmitted light; the Norwegian, brownish-green and darker. There is as little constant difference of colour between gadolinite and orthite as between the isotropic and anisotropic varieties, only that the latter contain paler spots. In most cases irregular flaws are observed, more seldom distinct laminated fissures, which, however, have no relation to the optical properties. The orthite from Hitteroe only exhibits interference colours, and only the allanite from Bastanäs shows pleochroism and strong absorption, but the latter property by itself was found more frequently.

The minerals are sometimes unaltered, in which case dark grains of an almost opaque body are found upon the flaws; at other times they are altered. The alteration begins chiefly at the surface in contact with accompanying minerals, and pierces thence into the interior. The slight agreement between the minerals, as well as in their crystalline form and optical properties, makes it difficult to draw general conclusions. The author, however, supposes that all gadolinites and orthites were originally infiltrated in a gelatinous state into cavities, and that they have partly remained in the amorphous condition, and partly assumed an internal crystalline structure. Consequently a mixture of dark isotropic and bright anisotropic parts is generally found, the latter being surrounded by a dark, almost opaque, but double-refracting zone.

It does not appear that the isotropic parts consist of the regular, and the anisotropic of changed mineral matter. G. T. A.

An Analysis of Meyonite. By E. NEMINAR (*Jahrb. f. Min.*, 1877, 942).—The author ascertained that wernerite contains small quantities of chlorine and carbonic acid (in addition to its other constituents), which are driven out only completely after strong ignition; it appeared, therefore, highly probable that meyonite would also contain the same bodies, and in order to confirm this supposition the author analysed a specimen of meyonite, with the following results, viz.:—

SiO_2.	Al_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Cl.	CO_2.
43·36	32·09	21·45	0·31	1·35	0·76	0·27	0·14	0·72 = 100·45

C. A. B.

The Sodium Felspar of Pantellaria. By H. FÖRSTNER (*Jahrb. f. Min.*, 1877, p. 942—944).—The greater part of the trachytic rocks of the island of Pantellaria are characterised by the presence of an unusually large amount of soda, pointing to the presence of a sodium felspar. Two varieties of this sodium felspar occur, differing from each other crystallographically and chemically; they are—

1. *Sodium Felspar from Cuddia Mida.*—This is found in the vitreous lava of the crater of Cuddia Mida in tabular crystals (through (∞Ꝑ∞), exhibiting the usual twin forms peculiar to orthoclase, particularly twins according to the Carlsbad law. Sp. gr. 2·55. A chemical analysis gave the following results:—

SiO_2.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	Na_2O.	K_2O.
66·63	0·72	19·76	0·38	0·30	7·31	4·86 = 99·96

2. *Sodium Felspar from Monte Gibele.*—Occurs in an andesitic rock in long prismatic crystals, the tabular type through ∞Ꝑ∞ being rare. Sp. gr. 2·61. Chemical composition as follows:—

SiO_2.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	Na_2O.	K_2O.
63·41	3·27	20·32	2·76	0·30	7·42	2·53 = 100·01

From this analysis it is evident that the specimen differs but very slightly from that of Cuddia Mida, there being a higher percentage of soda. Förstner found that the latter circumstance was in unison with the difference observed between the axial relations of its crystals and those of orthoclase, the prismatic angle approaching that of albite. Referring to the above analyses, the sodium felspar of Cuddia Mida is constituted as follows, viz.:—

$2\frac{1}{3}$ molecules of the combination $Na_2Al_2Si_6O_{16}$,
1 „ „ „ $K_2Al_2Si_6O_{16}$,

and that of Monte Gibele thus, viz.:—

1 molecule of the combination $Na_2Al_2Si_6O_{16}$,
1 „ „ „ $K_2Al_2Si_6O_{16}$.

They are therefore monosymmetrical felspars having the composition of albite, and containing only a secondary amount of the isomorphous potassium compound. The existence of such orthoclases is a proof of the dimorphism of the compound $Na_2Al_2Si_6O_{16}$, whilst the dimorphism of the corresponding potassium compound has been proved by the discovery of microline by Descloiseaux. Groth observed that the dimorphous modifications of potash felspar (potash-orthoclase and microline) exhibit an extraordinary closeness in their angular measurements, and it now appears, from Förstner's examinations of the sodium-felspars of Pantellaria, that a similar coincidence is observed in their angular measurements to those of the other dimorphous modifications of albite. C. A. B.

Occurrence of Astrophyllite, Arfvedsonite, and Zircon in El Paso Co., Colorado. By G. A. König (*Jahrb. f. Min.*, 1877, 944—946).—The three minerals are found imbedded in grey quartz, astrophyllite and zircon appearing inseparable, whilst arfvedsonite occurs isolated. The real matrix is probably syenite.

1. *Astrophyllite* is found in long, narrow, monosymmetrical prisms, without terminal faces. Cleavage very distinctly basal. H = 3. Spec. grav. 3·375. Colour on cleavage-planes, brass to bronze-yellow. Easily fusible before the blowpipe to a black bead, and decomposes in acids. An analysis furnished the following results:—

SiO_2.	TiO_2.	ZrO_2.	Fe_2O_3.	Al_2O_3.	FeO.	MnO.	K_2O.
34·68	13·58	2·20	6·56	0·70	26·10	3·40	5·01

Na_2O.	MgO.	CuO.	TaO_2.	H_2O.
2·54	0·30	0·42	0·80	3·54 = 99·83

Considering the percentage of water to be too high, we obtain the empirical formula $H_8(KNa)4(FeMn)9Fe_2{}^{vi}Fi_4Si_{13}O_{52}$.

2. *Arfvedsonite.*—The crystals of this mineral are long hexagonal prisms with the angles of hornblende. Cleavage prismatic and orthodiagonal. H = 6. Spec. grav. = 3·433. Raven-black, with a semimetallic lustre. Fuses easily to a black glass, but is scarcely attacked by acids. Chemical composition as follows:—

SiO_2.	TiO_2.	ZrO_2.	Fe_2O_3.	FeO.	MnO.	Na_2O,Li_2O.	K_2O.	MgO.	Loss on ignition.
49·83	1·43	0·75	14·87	18·86	1·75	8·33	1·44	0·41	0·20 = 97·87.

the empirical formula being $Na_6Fe_6Fe_4^{iii}Si_8O_{51}$.

3. *Zircon* occurs in microscopical shining brown or black crystals, imbedded in the quartz or astrophyllite. Type pyramidal, combination observed being P.∞P.0P, the latter rare face being present on all crystals from the above locality. Spec. grav. 4·538. Chemical composition as follows, viz.:—

SiO_2.	ZrO_2.	Fe_2O_3.	MgO.
29·70	60·98	9·20	0·30 = 100·18

Empirical formula = $Fe_2Si_{10}Zr_{19}O_{43}$. C. A. B.

Signification of the Rhombohedral and Prismatic Planes in Quartz.

By H. BAUMHAUER (*Jahrb. f. Min.*, 1877, 729—730).—By etching the planes very carefully with fused potassium hydrate the author has obtained impressions which are unsymmetrically formed to right and left, as well as above and below, and are not only different on +R and −R of one and the same crystal, but have also in right-handed and left-handed individuals an opposite position. The depressions on −R lie with their greatest breadth in the direction of the edge −R : ∞R; in right-handed crystals, however, the shortest side of the triangular impression is to the left above and to the right below; in left-handed crystals the reverse is the case. The surfaces +R are much less easily acted on by the alkali than −R. The impressions are triangular, and their greatest dimension lies in the direction of the combination edge of +R with the usual right or left trapezohedron $\frac{6P\frac{6}{5}}{4}$. On the prismatic surface ∞R, also, depressions were noticed which appear to have arisen from original six-sided forms by the rounding off of a corner. These are also unsymmetrical right and left, but whether the asymmetry extends to the upper and lower sides could not be determined with certainty. G. T. A.

Contributions to the Mineralogy of the Fassa- and Fleimser-Thal.

By C. DOELTER (*Jahrb. f. Min.*, 1877, 647—648).—This is a continuation of a former paper (this *Journal*, 1876, i, 877).

Analyses of fassaite: I, crystallised; II, crystalline from Toal della Foja; III, from the northern slope of Mal Inverno.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	H_2O.
I.	43·81	9·97	7·01	1·52	12·51	25·20	0·51
II.	44·06	10·43	5·91	1·67	13·10	25·20	0·15
III.	41·97	10·63	7·36	0·55	10·29	26·60	2·70

From these analyses it is clear that fassaite—at all events that of the Tyrol—holds an independent position, and does not belong to the aluminous augites.

New Locality for Contact-minerals, the Malgola in the Travignolothal.—The fassaite, hitherto known only from Monzoni, has been found at Malgola under similar conditions, *i.e.*, as a contact-mineral between monzonite and limestone. The fassaite, which occurs only in crystals, is accompanied by octohedrons of spinel and bright-green garnet in the combination $\infty O . 2O2$, as well as by serpentine.

Magnetite from Mulatto.—Fine crystals of this mineral are found on a solid mass of magnetite and exhibit the surfaces αO, $5O\frac{5}{3}$, $3O3.O$.

At Costa di Viezena, as products of contact of melaphyre and limestone, fine octohedrons of yellow garnet, and twins of the same are found, together with spinel and prismatic crystals of uralite.

Magnetite.—At Monte Common, where melaphyre is in contact with limestone, the latter has been converted into large laminæ of calc-spar and contains particles of solid magnetite. The pyrites which occurs at Monzoni in marble in contact with melaphyre shows combinations of $\infty O \infty$, $\frac{\infty O_2}{2}$, and $\frac{3O\frac{3}{2}}{2}$, in which the diakisdodecahedron sometimes prevails. The melaphyre from Mulatto contains in its cavities copper pyrites in fine crystals, $\frac{P}{2} - \frac{P}{2}$; adularia in simple and twin crystals; long prisms of apatite; pentagonal dodecahedrons of pyrites changed into brown-iron ore (limonite). G. T. A.

Thuringite from the Zirm-see in Carinthia. By V. v. ZEPHAROVICH (*Jahrb. f. Min.*, 1877, 732—733).—Peculiar forms of a mineral resembling chlorite occur in the weathered interstices of a felspar vein in the gneiss on the south-west shore of the Zirm-see. They are neither crystalline nor pseudomorphs, and consist of a fine-grained aggregate of a dark-green colour. Spec. grav. = 3·177. They give off water when heated, and melt before the blowpipe to a dark-green bead. They are decomposed by acids with separation of flakes of silica. Composition:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	H_2O.
22·65	18·92	8·12	38·49	10·78

The peculiar forms of these thuringites are thus explained. Inside and penetrating the thuringite are crystalline masses of felspar: when the thuringite was deposited between layers of calcite, these particles of felspar which projected into the cavities were enclosed by it. But felspar of later date than the thuringite is also found upon and among it in the cavities, and has been deposited after the removal of the calcite. This continued formation of felspar, after removal of the calcite, explains how it is that the thuringites are not sharply defined where they come in contact with the felspar, and often appear to be imbedded in it. G. T. A.

Analysis of the Warm Springs of Thermopylæ. By H. JAHN (*Deut. Chem. Ges. Ber.*, xi, 218—224).—The water of these springs is perfectly clear, tastes slightly saline, and smells faintly of hydrogen sulphide. Its temperature was found to be 39—40·9°, and its sp. gr. 1·0057 (water at 15·5° = 1).

The water contained in 10,000 c.c.:—

Calcium sulphate	7·1435	grams
Potassium chloride	2·2059	,,
Sodium chloride	65·7250	,,
Calcium chloride	8·7940	,,
Magnesium chloride	12·0230	,,
Calcium carbonate	7·9370	,,
Magnesium	0·7265	,,
Ferrous sulphide	0·0945	,,
Silica	0·3500	,,
Free carbon dioxide	2527·7	c.c.
Hydrogen sulphide	60·1	,,

J. R.

Organic Chemistry.

The more Volatile Products obtained from Crude Benzin (from Petroleum?). By C. VINCENT (*Compt. rend.*, lxxxvi, 340—342).—On rectifying crude benzin, a portion distils over below 80°. On standing this forms two layers, the heavier consisting almost entirely of carbon bisulphide. On re-distilling the upper layer, carbon bisulphide comes over below 75°, whilst the portion between 75° and 83° yields torrents of ammonia when treated with potash or soda, with formation of an acetate, and a liquid remains which, when distilled over lime, presents all the properties of anhydrous ethylic alcohol. The ammonia produced above is due to the decomposition of acetonitril (50 to 70 per cent. of the upper layer), which fixes the elements of water and gives rise to ammonia and acetic acid. The acetonitril could not be completely separated by mixing with fused and powdered calcium chloride and distilling. The carbon bisulphide obtained from the heavier layer can easily be purified by treatment with concentrated sulphuric acid; that obtained from the lighter layer contains a very small quantity of volatile hydrocarbons, difficult to separate. Some of them were separated by treating the distillate below 40° with alcohol and ammonia in a sealed tube over a vapour bath. After washing away the excess of alcohol and ammonia, and the ammonium thiocyanate formed, a liquid heavier than water was left, which, on distilling, yielded a mixture of hydrocarbons free from carbon bisulphide, absorbable by bromine, and rich in amylene. Methyl cyanide and carbon bisulphide occur in such proportions, that it might be advantageous to treat the lighter products of distillation industrially for the production of sodium and ammonium acetates. J. T.

Preparation of Amylene. By A. ETARD (*Compt. rend.*, lxxxvi, 488—490).—Wishing to obtain some kilograms of amylene, the author has modified the usual process, so as to avoid as much as possible the formation of polymerides, by removing the amylene formed as soon as possible from the sphere of action. For this purpose 500 grams of zinc chloride were placed in a large retort of glass, or preferably of metal, *e.g.*, an iron mercury bottle placed on a good gas furnace, and when the salt was perfectly fused a thin stream of the amylic alcohol was allowed to fall upon it. The alcohol employed was that obtained in the rectification of beetroot pulp, and contained, besides the two amylic alcohols, small quantities of propylic and butylic alcohols. The product froths a little, especially towards the end of the reaction, and as the vapour comes off with great rapidity, a long Liebig's condenser should be used. After desiccation of the condensed liquid by potassium carbonate, the amylene, which constitutes about one-third of the total volume, can be easily separated by distillation. The olefine when purified boils at 35—38°, and contains no trace of paraffin, as it is completely absorbed by bromine. Amylene thus obtained consists, with the exception of 2 or 3 per cent., of isopropyl ethylene, derived directly from isopropyl-ethyl alcohol by simple dehydration without molecular change, $(CH_3)_2CH.CH_2.CH_2OH = (CH_3)_2CH.CH{=}CH_2 + H_2O$. It is easily purified by agitation with sulphuric acid diluted with one-half its volume of water. The iodopentane, prepared by agitation of amylene in the cold with hydriodic acid, boils at 125°, which is 20° below the boiling point of its isomeride obtained from ordinary amyl alcohol. After the amylene has passed over, the succeeding fractions contain propylic alcohol boiling at 95—96°, butylic alcohol boiling at 108—109°, and ethylmethylethylic alcohol boiling at 128—129°; also diamylene boiling at 165°, and having a feeble odour of camphor. Other polymerides are also formed in this reaction, boiling at 230°, 300°, and 350°. These the author has not investigated. J. M. T.

On different Amylenes and Amyl Alcohols. By A. WISCHNEGRADSKY (*Liebig's Annalen*, cxc, 328—366)—Commercial amylene, prepared by the action of zinc chloride on fermentation amyl alcohol, is probably a mixture of three isomerides, viz., trimethylethylethene, unsymmetrical methylethylethene, and normal propylethene. It does not, however, contain any isopropylethene, this body at the moment of formation being converted into trimethylethene by the zinc chloride. When common amylene is treated with twice its weight of a mixture of equal volumes of water and sulphuric acid at a temperature of − 20°, half the hydrocarbon dissolves, forming amyl-sulphuric acid. The insoluble residue consists of amyl hydride (pentane) and amylene. The alcohol obtained from the amyl-sulphuric acid is identical with dimethylethyl-carbinol; it solidifies in a freezing mixture, forming crystals which melt at − 12°. It boils at 102·5°, and is oxidised by chromic acid to acetone.

Methylisopropyl-carbinol, prepared by the action of sodium amalgam on an aqueous solution of methylisopropyl-ketone, does not crystallise when cooled down in a freezing mixture of snow and calcium chloride. It boils at 112·5°, and on oxidation yields methylisopropyl-ketone.

The action of hydriodic and hydrochloric acid gas at 40° gives rise to tertiary instead of secondary halogen compounds, so that the hydrochloric or hydriodic acid must first deprive the alcohol of a molecule of water, and then unite with the amylene formed:—

$$CH_3.CH(OH).CH(CH_3)_2 - H_2O = (CH_3)_2C{=}CH(CH_3)$$
$$(CH_3)_2C{=}CH(CH_3) + HCl = CCl(CH_3)_2(CH_2.CH_3).$$

This view is confirmed by the fact that methylisopropyl-carbinol is decomposed into a mixture of amylenes and diamylenes by heating with dilute hydriodic acid in sealed tubes. The author considers that the amylene hydrate (b. p. 105—108°) of Wurtz and the alcohol (b. p. 104°) of Flavitzky are identical with dimethylethyl-carbinol. Ossipoff's statement (*Journ. Russ. Chem. Soc.*, iv, 236) that two different alcohols can be obtained by the action of dilute and of strong sulphuric acid on amylene was not confirmed.

That portion of the crude amylene which is insoluble in sulphuric acid unites with hydriodic acid at the ordinary temperature, forming an iodide which, on treatment with lead hydroxide yields an alcohol boiling at 117·5—119°. This alcohol is probably methylpropyl-carbinol, as it forms a ketone boiling at 101—103°, and this on oxidation splits up into acetic and propionic acids.

By the action of alcoholic potash on fermentation amyl iodide, a mixture of amylenes is obtained, boiling between 23° and 27°. After treatment with sulphuric acid, the hydrocarbon boils at 21·5°, and does not unite with hydriodic acid at 0°. When the mixture of amylenes boiling between 23° and 27° is saturated with hydriodic acid gas at − 20°, it forms tertiary amyl iodide boiling at 127—129°, and amylene boiling at 21·1—21·3°. The author regards this body, which unites neither with sulphuric acid nor hydriodic acid at 0°, as a secondary amylene, although it forms a tertiary iodide with hydriodic acid at the ordinary temperature.

Hydrobromic and hydrochloric acids act on the mixed amylenes in the same way, forming tertiary bromide boiling at 107—109°, or tertiary chloride boiling at 85—87°, and amylene boiling at 21—22°.

The crude amylene which boils between 23° and 27° is a mixture of two isomerides, viz., $(CH_3)_2CH.CH{=}CH_2$ and $(CH_3)(C_2H_5)C{=}CH_2$. The amylethyl-ether, obtained as a bye-product in the preparation of amylene from amyl iodide, is optically active. By treatment with hydriodic acid it is converted into ethyl iodide and optically inactive amyl iodide. From the latter body pure isopropylethene can be obtained. The isopropylethene in the mixture of amylenes owes its origin to the optically active amyl alcohol.

When the iodide formed by the union of hydriodic acid with isopropylethene is treated with alcoholic potash-solution, it yields an amylene boiling at 36°, identical with the trimethylethene of Jermolajeffs (*Liebig's Annalen*, clxii, 189).

According to the author, fermentation amyl alcohol consists chiefly of isobutyl-carbinol mixed with small quantities of normal amyl alcohol and methylethyl-carbinol. W. C. W.

Double Salts of Thallious Cyanide, and a New Thallium Cyanide.

By C. Fronmüller (*Deut. Chem. Ges. Ber.*, xi, 91—

95).—*Thallium and Silver Cyanide*, TlCN.AgCN.—White crystals, anhydrous, easily soluble in water, and much more stable than thallious cyanide. The solution is strongly alkaline. It is scarcely affected by carbon dioxide, but is decomposed by strong acids, silver cyanide being precipitated.

Thallium and Zinc Cyanide, $Tl_2C_2N_2.ZnC_2N_2$.—White crystals, easily soluble in water, forming an alkaline solution, which smells of hydrogen cyanide. When heated, the salt decrepitates and afterwards melts, undergoing complete decomposition.

Thallium and Mercury Cyanide, $Tl_2C_2N_2.HgC_2N_2$.—Colourless crystals of the regular system, freely soluble in water. Hydrogen sulphide passed into the solution throws down the metals as sulphides. Hydrogen chloride precipitates thallious chloride.

The foregoing salts were all obtained by dissolving the respective cyanides in solution of thallious cyanide.

Thallium Cobalticyanide, $(CN)_{12}Co_2Tl_6$, was obtained by digesting cobalt protoxide and thallious oxide in hydrocyanic acid at a gentle heat. It is an indistinctly crystalline yellow compound, moderately soluble in water, and is resolved by nitric and sulphuric acids into hydrogen cobalticyanide and the corresponding thallium salt.

Thallium Cyano-cyanide, $Tl_2C_4N_4$.—This salt is formed on dissolving moist thallic oxide in cold 20 per cent. hydrocyanic acid. It crystallises from the solution, on evaporation in a vacuum, in colourless anhydrous rhombic crystals, which dissolve easily in water. The formation of the salt is attended by the evolution of cyanogen and carbon dioxide, due to the following reactions:—

$$4Tl_2O_3 + 16HCN = 4Tl_2C_4N_4 + 8H_2O + 2O_2;$$
$$4HCN + O_2 = 4CN + 2H_2O;$$
$$2HCN + O_2 + 2H_2O = 2CO_2 + 2NH_3.$$

Thallium cyano-cyanide behaves like a compound of thallious and thallic cyanides ($TlCN + TlC_3N_3$), but it has not been found possible to obtain corresponding double salts in which the thallious cyanide is replaced by other cyanides. It is decomposed by even dilute acids, with liberation of hydrogen cyanide. Potash and moist mercuric oxide throw down thallic hydrate, leaving thallious hydrate in solution. Hydrogen sulphide reacts as follows:—

$$2Tl_2Cy_4 + 3H_2S = Tl_2S + 2TlSCy + 6HCy.$$

Salts of the heavy metals produce precipitates consisting of simple cyanides, thus:—

$$Tl_2Cy_4 + 4AgNO_3 = 4AgCy + TlNO_3 + Tl(NO_3)_3.$$

Potassium iodide reacts in the manner shown by the equation—

$$Tl_2Cy_4 + 3KI = 2\,TlI + ICy + 3KCy.$$

J. R.

Conversion of Cyanamide into Ammelide. By C. O. CECH and B. DEHMEL (*Deut. Chem. Ges. Ber.*, xi, 249—251).—The authors heated cyanamide to 100° in a sealed tube with cyanogen bromide, expecting to obtain dicyanamide, but the bromide remained unaltered, at any rate in part. On treating the contents of the tube with boiling water, there was left undissolved a yellowish-white substance, which dissolved in boiling hydrochloric acid, and was deposited on cooling in the form of a snow-white crystalline powder, having the composition and properties of ammelide, $C_3H_4N_4O_2$. It appears, therefore, that cyanogen bromide does not act upon cyanamide, but that the latter substance is converted by heat into a body isomeric with melamine, which is then resolved by the action of water and hydrochloric acid into ammonia and ammelide. J. R.

Preparation of Thiamides. By A. W. HOFMANN (*Deut. Chem. Ges. Ber.*, xi, 338—340).—The author obtains excellent results in the preparation of thioformanilide and thiacetanilide by the action of phosphorus sulphide on the corresponding oxygen-compounds. By the same method acetamide is converted into the corresponding sulphur-compound, and it appears to be generally applicable to both simple and substituted amides.

The author also announces the preparation by this method of the long sought thioformamide, and is proceeding with its investigation. C. F. C.

Introduction of Nitrogenous Radicles into Members of the Fatty Group. By V. MEYER (*Deut. Chem.-Ges. Ber.*, x, 2075—2078).—*Azophenyl-aceto-acetic acid*, $CH_3.CO.CH(N_2.C_6H_5)COOH$, is prepared by acting with a dilute solution of diazobenzene nitrate on ethylic aceto-acetate dissolved in potassium hydrate. The mixture is rendered alkaline by the addition of dilute potassium hydrate solution, and filtered to remove resinous matter. On acidifying the filtrate with dilute sulphuric acid, azophenylaceto-acetic acid is thrown down in the form of a bulky yellow precipitate.

The pure substance dissolves in alkalis and in alcohol, forming yellow solutions. Golden tabular crystals, melting at 154—155°, are deposited on evaporating the alcoholic solution.

By the action of nitrous acid on ethylic aceto-acetate, a transparent oily liquid, heavier than water, is obtained, which is soluble in alkalis, forming a yellow solution. It cannot be distilled without decomposition, and is also decomposed by boiling with hydrochloric acid. The composition of this substance is $C_6H_9O_4N$, and as its formation is analogous to that of nitroethane, its constitution is probably $CH_3.CO.C{=}(N.OH)COOC_2H_5$, or it may be regarded as a nitroso-compound, $CH_3.CO.CH(NO)COOC_2H_5$. The author intends to study the action of nitrous acid on methyl and ethyl acetoethyl-acetates.

W. C. W.

Some Cyamides of Acid Radicles. By O. MERTENS (*J. pr. Chem.*, xvii, 1—38).—Sodium cyamide and acetic anhydride give sodium-acetyl cyamide, according to the following equation:—

$$2(CN.NHNa) + (C_2H_3O)_2O = CN.N(C_2H_3O)Na + C_2H_3ONa + CNNH_2.$$

12 grams of sodium cyamide were dissolved in 700 c.c. of hot anhy-

drous ether, and the acetic anhydride added, mixed with its own bulk of ether. The reaction is complete in 3—4 hours. The residue, after repeated digestion with ether to remove cyanamide, consisted of sodium acetate and *sodium-acetyl-cyamide*. It was dissolved in water, and converted by silver nitrate into *silver-acetyl-cyamide*. To separate the silver-acetyl-cyamide from silver-cyamide the silver salts were digested with ammonia, in which the former alone dissolves, and reprecipitated with dilute nitric acid. It forms a white insoluble substance, and on heating gives off a smell of acetonitril. Silver-acetyl-cyamide when suspended in ether and decomposed with sulphuretted hydrogen yielded silver sulphide and a yellow syrup with an acid reaction, soluble in ether, alcohol, and chloroform, but not in benzene. It was proved to be *acetyl-cyamide*, by converting it into the silver compound, which on analysis gave the formula $CN.N(C_2H_3O)Ag$. By digesting the silver compound with sodium chloride, *sodium-acetyl-cyamide*, $CN.N(C_2H_3O)Na$, was formed. On adding ether to its alcoholic solution it separated in fine needles. It is also obtained by treating with sodium carbonate the chloride of acetyl-cyamide, prepared by digesting cyamide with acetyl chloride. Sodium-acetyl-cyamide probably undergoes the following decomposition when heated:—

$$CNN(C_2H_3O)Na = CH_3CN + CNONa.$$

A potassium compound was also prepared, which resembled the sodium compound in every respect.

Diacetyl-cyamide was prepared by digesting silver-acetyl-cyamide with acetyl chloride in presence of absolute ether. Its formula is $CN.N(C_2H_3O)_2$. It is insoluble in water, and crystallises from alcohol or ether in white rhombic tables. It decomposes completely at 75°. An attempt was made to obtain diacetyl-cyamide by digesting copper cyamide with acetyl chloride, but on evaporating the ether with which the reacting bodies were diluted, crystals of acetyl-urea were deposited, thus rendering it probable that the formula of copper cyamide is $CN.NH(CuO) + H_2O$, the reaction being:—

$$CN.NH(CuO).H_2O + 2CH_3COCl =$$
$$CuCl_2 + CO\left\{\begin{matrix}NH.COCH_3\\NH_2\end{matrix}\right. + CH_3COOH.$$

Butyryl-cyamide was prepared in a similar manner by treating sodium-cyamide with butyric anhydride in presence of ether. It was purified in the same manner as the acetyl-cyamide, but owing to the sparing solubility of silver butyrate, it was necessary to dissolve the silver salt several times in ammonia and throw it down with nitric acid. Its formula is $CN.N(C_4H_7O)Ag$. It is a white, indistinctly crystalline powder. The sodium compound was also prepared and analysed. It crystallises well, is easily soluble in water, less easily so in alcohol, and is insoluble in ether.

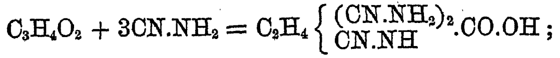
Valeryl-cyamide.—The silver salt was prepared by the process already given. This was converted into valeryl cyamide—

$$CN.N(C_5H_9O)H,$$

by suspending it in ether and treating it with sulphuretted hydrogen.

It formed a syrup, which was analysed, and gave numbers corresponding to the above formula.

Action of Lactide on Potassium Cyamide.—It was expected that this reaction would yield melidopropionic acid, thus—



$$C_3H_4O_2 + 3CN.NH_2 = C_2H_4\left\{\begin{matrix}(CN.NH_2)_2 \\ CN.NH\end{matrix}\right..CO.OH\,;$$

melidoacetic acid having been prepared by Drechsel by the action of monochloracetic ether on sodium cyamide. By the action of 13·5 grams of potassium cyamide, dissolved in alcohol on 24 grams of lactide, white tabular crystals were deposited, having the empirical formula $C_4H_6O_2N_2$, but probably consisting of lactyl-cyamide,

$$CN.NH.C_2H_4(OH)CO.$$

It dissolves with difficulty in cold water, is easily soluble in hot water and in alcohol, and insoluble in ether. It melts at 212°, and solidifies to stellate groups of crystals on cooling. Its silver compound, obtained by treatment with silver nitrate, is a curdy precipitate of the formula $C_4H_5AgN_2O_2$. W. R.

Use of Dehydrated Oxalic Acid to distinguish the Polyatomic Alcohols. Chemical Function of Inosite. By M. Lorin (*Compt. rend.*, lxxxiv, 1136—1139).—Having studied the action of glycerin, erythrite, and mannite on crystallised and on dehydrated oxalic acid, the author proceeds to investigate the action of dulcite, quercite, and inosite on the same substances.

Dulcite.—43 grams of dulcite were treated with successive portions of crystallised oxalic acid, and the distillate collected in small fractions. The first portions contained about 23·0 per cent.; the last 56·5 per cent.; and the whole mixed distillate 51·6 per cent. of pure formic acid. Altogether, 740 grams of acid were obtained. In another experiment 3·78 kilos. of oxalic acid furnished 2·23 kilos. of formic acid of 48·6 per cent.; that is, containing 1·085 kilos. of real acid.

In operating upon dulcite with dehydrated oxalic acid, it is better to start with the crude formin resulting from a previous operation. Thus, with the formin from 61 grams of the alcohol, by the addition of dry acid in portions of 100 grams at a time, a united distillate was obtained containing 89 per cent. of formic acid, of which some of the separate fractions rose as high as 94 per cent. The retort still contained an acid of 80 per cent., which, on distillation in a water-bath, furnished distillates less and less rich in formic acid, while carbon monoxide was continually disengaged.

Quercite gave results perfectly analogous to the foregoing, with somewhat less facility. With crystallised acid, a formic acid was prepared, the maximum strength of which was 59 per cent.; with the dehydrated acid the maximum strength of the resulting product was 89 per cent., and the mean of the whole operation 73·6 per cent. The carbon dioxide evolved was never free from carbon monoxide, the latter generally forming about 10 to 20 per cent. of the total gas.

Inosite, in like manner when distilled with ordinary oxalic acid, yielded a formic acid of 53 per cent. (maximum), and with dehydrated acid a similar product as high as 75 per cent. In the latter case the carbon dioxide was mixed with carbon monoxide, and the tendency to decomposition at the required temperature prevented the percentage from rising to a higher figure. These reactions, however, are sufficient to show that inosite is unquestionably a polyatomic alcohol, closely allied in its chemical relationships to quercite.

Other saccharine substances, such as cane-sugar, dextrose, sugar of milk, and sorbin, react with oxalic acid in a manner altogether different from that of the polyatomic alcohols. When mixed with the acid and heated to a regulated temperature, they produce neither carbon dioxide nor formic acid, but the mixture swells up and becomes coloured; after prolonged heating, the whole is finally charred and decomposed. J. W.

Identity of Muscular Inosite and Vegetable Sugars of the same Composition. By MM. TANRET and VILLIERS (*Compt. rend.*, lxxxvi, 486—488). — The authors have already shown the identity of inosite with sugar from walnut leaves and French beans. Since then they have become acquainted with the sugar extracted from ash leaves by Gintl, which is also identical with the others, both in composition and crystalline form. For the purposes of comparison, they have measured the angles of the crystals derived from these various sources with those of inosite extracted from horse-flesh. These measurements are given in a table, and are practically identical.

The crystals of inosite obtained from horse-flesh were too imperfect to allow of many measurements being made. Those obtained, however, the authors consider sufficient to show the identity of this sugar with the others. The specific gravity of the inosite from walnut leaves was found to be at 15° C., 1·524; that from horse-flesh, 1·535 at 8° C.; that from French beans gave an identical result. It would, therefore, appear that inosite is very widely distributed in nature, Marmè having shown that peas, green beans, acacia, cabbage, digitalis, potato plant, asparagus, and two cryptogams, also contained sugar of the same kind. It would, however, be necessary to examine them crystallographically, to establish their identity with the others. The authors draw attention to the fact that inosite is always accompanied by glucose in urine; and that extracted from walnuts or French beans is always found crystallised in a fermentable saccharine liquid which reduces Fehling's solution. J. M. T.

Quercite a Pentad Alcohol. By F. W. HOMANN (*Liebig's Annalen*, cxc, 282—294).—When quercite is heated with an excess of acetic anhydride for 8—10 hours at 100—120°, an amorphous, very hygroscopic mass is obtained, consisting of *quercite pentacetate*, $C_6H_7(OC_2H_3O)_5$. The same compound is formed by heating quercite with an excess of acetyl chloride at 100°. On heating quercite on a water-bath with two to three parts of the anhydride until all is dissolved, the *tetracetate* $C_6H_7OH(OC_2H_3O)_4$ is formed, which closely resembles the preceding compound. By using 1·6 parts of quercite, 10 parts of acetic acid, and 1 of the anhydride, and heating at 170° for 10 hours, the *diacetate* $C_6H_7(OH)_3(OC_2H_3O)_2$ is formed, which is also an amorphous, hygroscopic body.

By the action of a mixture of one part of concentrated nitric acid and 10 parts of sulphuric acid, *quercite pentanitrate* is obtained, which is an almost colourless resinous mass, insoluble in water, but readily soluble in absolute alcohol and in ether. It explodes on heating. Quercite is not altered by heating it with concentrated hydrochloric acid under pressure at 100°. C. S.

Compounds of Quercite. By L. PRUNIER (*Compt. rend.*, lxxxvi, 338—340).—By the action of hydrochloric acid on quercite, one, three, or five molecules of water are replaced by a corresponding number of molecules of hydrochloric acid, according to the strength of the acid, and the temperature to which it is heated.

Quercite heated at 100° for three or four days with hydrochloric acid, saturated at 10°, yields a monochlorhydrin, $C_6H_{10}O_4.HClO_4$, in small quantity, as a white crystalline body, soluble in ether and in alcohol, but is decomposed by the latter and also by water. It melts between 198—200°. At the same time a viscous substance is formed, which is colourless when cold, but turns brown on heating. It is soluble in cold absolute alcohol, and from its analyses appears to be quercitane monochlorhydrin, $C_6H_8O_3HCl$.

At 115°, with hydrochloric acid of the same strength, quercite trichlorhydrin, $C_6H_6O_2.3HCl$, is formed. It crystallises in long flat needles, which darken in colour when exposed to the air, and melt at 155°.

By the continued action of hydrochloric acid on the trichlorhydrin, quercite pentachlorhydrin ($C_6H_2.5HCl$) is formed in long slender needles, which are soluble in alcohol, ether, and benzene, and melt at 102°. Its empirical formula, $C_6H_7Cl_5$, is related to that of benzene hexchloride, $C_6H_6.Cl_6$, one atom of chlorine in which is replaced by hydrogen.

On exhausting the residue (which remained on evaporating the mother-liquor, from which the above bodies were obtained, to dryness) with alcohol, a body corresponding to quercitane monochlorhydrin was obtained, which, when treated with sulphuric acid, gives rise to an amorphous, colourless body, very deliquescent and soluble in alcohol; this, on analysis, gave numbers corresponding with the formula of quercitane, $C_6H_{10}O_4$. L. T. O'S.

Decomposition of Trimethylamine Hydrochloride by Heat. By C. VINCENT (*Compt. rend.*, lxxxiv, 1139, 1140).—When an aqueous solution of trimethylamine hydrochloride is heated, its boiling point gradually rises until it reaches 260°. At this temperature it begins to decompose, evolving abundance of gaseous products, whilst a small portion of the original substance sublimes.

In order to examine the products of decomposition, the gaseous portion, which was strongly alkaline, was passed into dilute sulphuric acid, in which it partly condensed. The permanent gas, which was present in large quantity, was separately examined and found to be methyl chloride; the condensed portion, on analysis of its chloroplatinate, proved to be pure trimethylamine.

This decomposition proceeds regularly up to 285°, the contents of the retort at that temperature being a mixture of mono- and trimethylamine hydrochlorides. At 305° the mixture has altered, and is then composed of monomethylamine hydrochloride and sal-ammoniac; at 320° or 325° everything has sublimed, the sublimate consisting entirely of the last-mentioned substances. By exhausting either of the last two products with absolute alcohol, a solution of pure monomethylamine hydrochloride can be obtained.

The author thinks that, inasmuch as trimethylamine hydrochloride is obtainable in considerable quantity as a bye-product in some industries, it may be conveniently used either as a source of methyl chloride, or directly as a means of methylating aniline, since when it is heated with that substance, methyl-aniline is produced. J. W.

Catalytic Action of Carbon Bisulphide on Mixtures of Bromine and Acetic or Formic Acid. By C. HELL and O. MÜHLHÄUSER (*Deut. Chem. Ges. Ber.*, xi, 241—246).—In continuing the experiments on this subject described in a former paper (*Deut. Chem. Ges. Ber.*, x, 2102), the authors have found that carbon bisulphide not only induces the formation of addition-compounds, but also greatly facilitates the production of substitution-compounds, this induced action being the more rapid the greater the quantity of bisulphide present. In all cases, the formation of addition-compounds precedes that of substitution-products.

Experiments with formic acid seem to show that it behaves in the same manner as acetic acid, forming with bromine first an addition-compound and afterwards a substitution-product, which latter, however, breaks up as fast as it is formed into carbon dioxide and hydrogen bromide. J. R.

Formation of Acid Bromides by the Addition of Oxygen to Brominated Olefines. By E. DEMOLE (*Deut. Chem. Ges. Ber.*, xi, 315—320).—*Dibromethylene* is converted, by agitation with dry oxygen gas, into *monobromacetyl bromide:*

$$BrHC{=}CHBr + O = CH_2Br.COBr,$$

the reaction being attended with a rise of temperature from 15° to 55°.

Tribromethylene, under the same conditions, also unites with 1 at. oxygen, with formation of *dibromacetyl bromide*.

$$Br_2C{=}CHBr + O = CHBr_2.COBr.$$

In the preparation of tribromethylene from the compound $CHBr_2.CHBr_2$, the author finds that by the action of alcoholic potash upon the latter, monobromacetylene and dibromethylene are also formed. The best results are obtained by decomposing the tetrabromethane with an alcoholic solution of potassium acetate in presence of sodium carbonate.

Tribromethylene, prepared by either method, boils at 162° and not at 130°, as stated by Lennox. Its sp. gr. at 0° is 2·69. C. F. C.

Trichloracetic Anhydride. By A. CLERMONT (*Compt. rend.*, lxxxvi, 337).—By the successive action of phosphorus pentoxide and trichloracetyl chloride on trichloracetic acid, a colourless liquid is formed, which readily attracts water and boils at 223°, the reaction being—

$$C_2Cl_3O.HO + C_2Cl_3O.Cl = (C_2Cl_3O)_2O + HCl.$$

It is probably identical with the trichloracetic anhydride of Buckney and Thomsen (*Ber.*, x, 698), which is formed by a secondary reaction when phosphorus trichloride acts on trichloracetic acid.

L. T. O'S.

Bromomucic Acid. By O. R. JACKSON and H. B. HILL (*Deut. Chem. Ges. Ber.*, xi, 289—292).—According to Schmelz and Beilstein, when bromomucic acid is boiled with baryta water, it is resolved into carbonic acid, monobromacetylene, and the barium salt of muconic acid, $C_4H_2O_3$, which is difficultly soluble in cold water. This reaction takes place as follows:—

$$2C_4H_2Br_2O_3 + H_2O = C_4H_2O_3 + C_2HBr + 2CO_2 + 3HBr.$$

The authors find by a quantitative study of this reaction that, with quantities of baryta increasing from 2¼ to 6 molecules to each molecule of bromomucic acid, the quantity of the difficultly soluble barium salt increases, whilst the amounts of barium carbonate, hydrobromic acid, and hydrocarbons decrease in the same proportion. The bromacetylene and hydrobromic acid were absorbed by passing the gases through an ammoniacal solution of cuprous oxide, and determined, the former by the amount of hydrocarbons set free by heating the red compound formed with hydrochloric acid; the latter by the amount of ammonium bromide produced.

The further study of the so-called muconic acid formed by the action of baryta-water on bromomucic acid, and the analysis of its lead salt, which is obtained as a white precipitate on adding lead acetate to its barium salt, shows that the acid in question is really malonic acid, and that the lead salt has the composition, $PbC_3H_2O_4$. The lead salt on standing becomes crystalline, the crystals consisting of small rhombic plates. The silver salt is obtained in the form of small, short needles. The acid prepared from the lead salt by the action of sulphuretted hydrogen is easily soluble in water, and crystallises from its aqueous solutions in rhombic, leafy tables, which melt at 131·5°—132°, as found by Heintzel (*Ann. Chem. Pharm.*, cxxxix, 132).

The authors have likewise found that by the action of baryta-water on bromomucic acid, barium bromide and barium formate are produced, and think that the following equation is the most probable expression of the reaction:—

$$C_4H_2Br_2O_3 + 3H_2O = C_3H_4O_4 + CH_2O_2 + 2HBr.$$

P. P. B.

Decomposition of Acetoacetic Ethers. By J. WISLICENUS (*Liebig's Annalen*, cxc, 257—281).—The author has already shown, that by the action of alkalis on these ethers, not only ketones, carbon dioxide, and alcohol are formed, as Duppa and Frankland have found, but also that a certain portion is resolved into acetic acid and a substituted acetic acid. In order to ascertain under what conditions these reactions take place, he has made a great number of experiments, from the results of which he concludes that ketones are chiefly produced when the ethers are boiled with baryta-water or a dilute solutions of caustic potash, whilst an excess of concentrated alkali yields principally fatty acids. Ethylic ethylacetoacetate yields ketones more readily, and acids less easily than ethylic diethylacetoacetate, whilst the ethylic ethers of methylacetoacetic and dimethylacetoacetic acids behave just in the opposite way. C. S.

Action of Sodium on Ethyl Ethoxyacetate. By M. CONRAD (*Deut. Chem. Ges. Ber.*, xi, 58—60).—Ethylic ethoxyacetate, diluted with an equal bulk of benzene, and gently heated over the water-bath, dissolves about 16 per cent. of its weight of sodium, evolving hydrogen, and turning thick and brown. The product, after treatment with acetic acid, yields by distillation an oily body, boiling at about 245°, and agreeing in composition with the formula, $C_{10}H_{18}O_5$. The author believes this substance to be *ethylic ethoxyacetyl-ethoxyacetate*, $CH_2OC_2H_5.CO.CHOC_2H_5.COOC_2H_5$, and that it is formed by a reaction precisely analogous to that by which ethylic aceto-acetate is formed from ethyl acetate.

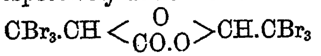
The compound gives a fine violet coloration with ferric chloride. It dissolves sodium, and forms a barium-compound insoluble in water. When boiled with acids, it gives off carbon dioxide; and when heated with alkalis it is resolved into ethoxyacetates and ethyl alcohol.

J. R.

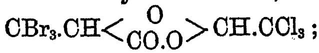
Oxidation-Products of Stearolic Acid. By L. LIMPACH (*Liebig's Annalen*, cxc, 294—304).—Pure oleic acid from oil of almonds was converted into the dibromide by Overbeck's method, and heated with a solution of 4 mols. of potash in alcohol for 12 hours in a flask connected with a reversed condenser. On decomposing the product with hydrochloric acid, pressing the crystalline mass between filter paper, to remove some monobromoleic acid, and crystallising from alcohol, pure stearolic acid, melting at 46°, was obtained. The monobromoleic acid produced in the reaction was heated with alcoholic potash at 150° for 6—8 hours, and thus a further yield of stearolic acid was obtained.

By oxidising stearolic acid with fuming nitric acid, Overbeck obtained stearoxylic acid, $C_{18}H_{32}O_4$, azelaic acid, $C_9H_{16}O_4$, and the aldehyde, $C_9H_{16}O_3$ of the latter; but on repeating this experiment and separating the product by Overbeck's method, the author obtained azelaic acid, stearoxylic acid, pelargonic acid, and nitrosopelargonic acid, $C_9H_{18}O_2(NO)_2$, which was discovered by Chiozza, but could not detect an aldehyde of azelaic acid among the products. C. S.

Tribromolactic Acid, Bromalide, and β-Monobromacrylic Acid. By O. WALLACH and J. REINECKE (*Deut. Chem. Ges. Ber.*, x, 2128—2132).—When tribromolactic acid is prepared by Pinner's process, and carefully purified, it forms a crystalline mass, melting at 141—143°; the crude acid, however, is fluid. The ethylic ether, $CBr_3.CH(OH).COOC_2H_5$ crystallises in needles. Similarly the tribromethylidene and trichlorethylidene ethers are solid bodies, fusing respectively at 158° and 132—135°, and indicated by the formulæ,

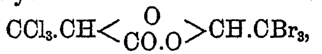


$CBr_3.CH<\substack{O \\ CO.O}>CH.CBr_3$ and



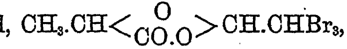
$CBr_3.CH<\substack{O \\ CO.O}>CH.CCl_3$;

whilst the tribromethylidene ether of trichlorolactic acid,



$CCl_3.CH<\substack{O \\ CO.O}>CH.CBr_3$,

isomeric with the latter, melts at 149—150°, and the tribromethylidene ether of lactic acid,



$CH_3.CH<\substack{O \\ CO.O}>CH.CHBr_3$, at 95—97°.

When the chloralide of tribromolactic acid, fusing at 132—135°, is submitted to the action of reducing agents, it does not form dibromacrylic acid as might be expected, but gives rise to *monobromacrylic acid*, melting at 115—116°, after crystallisation from ether or chloroform, and forming a silver salt crystallisable from dilute alcohol. This acid must necessarily possess the constitution, $CHBr{=}CH.COOH$, *i.e.*, it is the β-acid; Philippi and Tollens have found that the α-acid, $CH_2{=}CBr.COOH$ (prepared from α-dibromopropionic acid), melts at 69—70°, whilst Wagner and Tollens describe the β-acid (from β-dibromopropionic acid) as melting at the same temperature as the α-acid, and much resembling it; whence it appears that the bromacrylic acid of these latter chemists really was the α-acid, which may result by depriving β-dibromopropionic acid of the elements of HBr just as readily as β-bromacrylic acid.

The chloracrylic acid obtained by Pinner from trichlorolactic acid, and by the authors from the chloralide of that acid, melts at 84—85°, and is clearly the β-acid, $CHCl{=}CCl.COOH$, whilst the acid prepared by Beckurts and Otto from α-dichloropropionic acid, is necessarily the α-acid, $CH_2{=}CCl.COOH$; they describe the acid as fluid, and boiling at 176—181°. Since the acid prepared by Werigo from β-dichloropropionic acid, and fusing at 64—65°, is presumably not the β-chloracrylic acid, but the α-acid (by analogy with the bromo-acid), it would seem that Beckurts and Otto's product was slightly impure, and hence did not crystallise readily, and that probably, if it were obtained crystallised, the crystals would melt at 64—65°. C. R. A. W.

New Products from Coal Gas. By L. THOMPSON (*Chem. News*, xxxvii, 95).—When coal gas, containing a large proportion of carbon bisulphide has been passed for some days through a solution of mercuric cyanide in caustic potash, a white precipitate is produced, and on continuing the current of gas, the precipitate finally becomes of a beautiful scarlet colour. The production of this body was found to be due to the presence in the coal gas of carbon bisulphide, from which it can be prepared directly, by boiling mercuric oxide with a solution of potassium cyanide, adding a strong solution of the hydrate, and when cold, agitating with carbon bisulphide, and gently warming. When washed and dried, it resembles vermilion in colour, but the tint is not so violet. It sublimes on the application of heat to a jet-black mass, but re-acquires the red colour when it is finely powdered. It is unaffected by acids, except aqua regia, and is not altered in colour by hydrogen sulphide. It is suggested to call this body ponsælion. The white precipitate which is first formed on adding the bisulphide, consists, when washed and dried, of a grey-white powder, which explodes with great violence when it is heated to about 400° F., depositing much soot-like substance; it is called *cyanone*. The cyanogen-compound, which in cyanone is united to mercury, has been transferred to copper, forming an equally explosive substance, but which is destroyed by ammonium hydrosulphide. A. J. C.

Action of Carbonyl Chloride on Toluene, in Presence of Aluminium Chloride. By E. Ador and J. Crafts (*Deut. Chem. Ges. Ber.*, x, 2173).—When toluene (200 grams) and carbonyl chloride (130 grams) are mixed (by absorption of the gas), and aluminium chloride added little by little, for ten minutes, paratoluyl chloride is formed; for on adding water, shaking the acid liquid with ether, and the benzene solution with potash, and working up the two extracts together, paratoluic acid, melting at 177—178°, is produced, the reaction being parallel to that previously shown to take place with benzene:—

$$C_6H_5(CH_3) + COCl_2 = HCl + C_6H_4\left\{\begin{matrix}CH_3\\COCl\end{matrix}\right..$$

When the reaction is pushed on as far as possible, *diparatolyl ketone*, $CH_3.C_6H_4.CO.C_6H_4.CH_3$, is formed. This compound boils at 333—333·5° (not corrected), and by oxidation with chromic acid is converted into *tolylbenzoic acid*, $CH_3.C_6H_4.CO.C_6H_4.COOH$, melting at 228°, and a benzophenone-dicarbonic acid, $COOH.C_6H_4.CO.C_6H_4.COOH$, melting and subliming at upwards of 300°. No benzoic, α-toluic, or phthalic acid is formed, proving the absence of ketones of the forms $C_6H_5.CH_2.CO.CH_2.C_6H_5$, or $C_6H_5.CH_2.CO.C_6H_4.CH_3$. On fusion with caustic potash for some hours, almost the theoretical quantity of paratoluic acid is formed. C. R. A. W.

Oxidation of Ethyltoluene. By H. N. Morse and Ira Remsen (*Deut. Chem. Ges. Ber.*, xi, 224—229).—Para-ethyltoluene treated with bromine yields a substitution-compound, which is converted by oxidation with chromic acid into bromoparatoluic acid, identical with that described by Jannasch and Dieckmann (*Liebig's Annalen*, clxxi, 84). The authors assign to the substitution-compound the formula, $C_6H_3.CH_3 : Br : C_2H_5 = (1 : 2 : 4)$. The oxidation of the ethyl- and not of the methyl-radicle in this compound, is supposed to be due to the fact that the latter occupies a position adjacent to the bromine-atom, and is thereby protected from oxidation. J. R.

Nitro-compounds. By A. Laubenheimer (*Deut. Chem. Ges. Ber.*, xi, 303—306).—The author has previously shown (*Deut. Chem. Ges. Ber.*, ix, 1826) that caustic soda and ammonia decompose orthodinitro-derivatives, replacing one of the nitro-groups by hydroxyl or by NH_2. In the present paper, he shows that by the action of ammonia on dinitrochlorobenzene, nitrochloraniline and ammonium nitrite are formed, and not, as might be expected, from the formula for the nitro-group, $—N<^{O}_{O}>$, an isomeride of ammonium nitrite, derived from the acid, $H—N<^{O}_{O}>$.

W. C. W.

Action of Iodine Chloride on Aromatic Amines. By A. Michael and L. M. Norton (*Deut. Chem. Ges. Ber.*, xi, 107—116).—The authors give an historical sketch of the use of iodine chloride to prepare iodo-substitution-compounds. Its use for this purpose was first proposed by Schützenberger, who, by its action on sodium benzoate, obtained moniodo- and diiodo-benzenes.

An acetic acid solution of acetanilide, treated with one molecule of iodine chloride, yields *iodoacetanilide* as a dark crystalline precipitate. Iodoacetanilide, $C_6H_4I.NHC_2H_3O$, dissolves easily in hot water, crystallising from such solutions in white rhombic plates; alcohol and glacial acetic acid dissolve it also. It melts at 181·5°. By boiling it with hydrochloric acid and treating the salt so formed with ammonia, moniodaniline, melting at 60°, is obtained, showing that iodine chloride acts in a similar manner to bromine and chlorine, producing a para-compound.

Para-iodo-acetanilide is decomposed by concentrated nitric acid, with separation of iodine. When a solution of the acetanilide in glacial acetic acid is treated with nitric acid, however, it yields a nitro-iodanilide, which crystallises from alcohol in orange-yellow needles, and melts at 122°. Para-iodo-nitranilide, $C_6H_5IN_2O_2$, dissolves only sparingly in water, more freely in alcohol and glacial acetic acid, and does not unite with hydrochloric acid to form salts.

Iodine chloride reacts on acetanilide so as to produce only moniodo-compounds; its action on a solution of aniline in glacial acetic acid is, however, different, a mixture of moniod- and di-iodanilines being produced. The di-iodaniline is separated from the mono-derivative by distilling it in a current of steam. $C_6H_3I_2.NH_2$ crystallises from its alcoholic solutions in long white needles, melting at 95—95·5°, and solidifying again at 63°. It is insoluble in water, but soluble in alcohol and glacial acetic acid. Its basic properties are very feeble, the hydrochloride being decomposed by water into base and hydrochloric acid.

By the action of 3 mol. of iodine chloride on 1 mol. of aniline dissolved in hydrochloric acid, tri-iodaniline, $C_6H_2I_3.NH_2$, is formed, which crystallises from glacial acetic acid in long white needles, melting at 185·5°, and solidifying again at 146°. It is insoluble in water, dissolves in hot hydrochloric acid, from which solution it separates on cooling; hot alcohol and carbon bisulphide also dissolve it. Tri-iodaniline is volatilised by a current of steam; it is identical with a product obtained by Stenhouse in a somewhat similar manner (*Ann. Chem. Pharm.*, cxxxiv, 213).

By the action of 3 mol. iodine chloride on 1 mol. of meta-nitraniline, dissolved in hydrochloric acid, di-iodometanitraniline, $C_6H_4I_2N_2O_2$, is obtained, which crystallises from hot alcoholic solutions in long needles, insoluble in acetic ether, and melting at 145·5°. It possesses feeble basic properties, and dissolves in nitric acid without separation of iodine. A moniodo-nitraniline appears to be formed at the same time; it is soluble in acetic ether, which property may be used to separate it from the diodo-compound: it crystallises in tabular crystals, and melts between 85° and 95°.

When 3 mol. of iodine chloride react on 1 mol. of paranitraniline dissolved in hydrochloric acid, two substituted iodo-compounds are formed, which are separated by their different solubilities in hot water.

Moniodo-paranitraniline, $C_6H_5N_2IO_2$, is easily soluble in hot water, crystallising from its aqueous solution in canary-yellow needles, which dissolve easily in hot alcohol, and melt at 105·5°. Its hydrochloride is decomposed by water.

Di-iodo-paranitraniline, $C_6H_4I_2N_2O_2$, is difficultly soluble in hot water, and is formed only in small quantities. It is obtained alone, when 2 mol. of iodine chloride act on 1 mol. of paranitraniline dissolved in chloroform. It crystallises from alcohol in bright yellow needles, which exhibit a blue reflection, and melt at 243—244°. Chloroform, acetic ether, and nitrobenzene dissolve it. It possesses no basic properties.

Di-iodo-paratoluidine, $C_7H_7I_2N_2$, is obtained by the action of iodine chloride on a solution of paratoluidine in hydrochloric acid; it crystallises from alcohol in long branching needles, melting at 124·5°, and is slightly soluble in hot water, and easily in alcohol. P. P. B.

Action of Acid Chlorides on Amido-derivatives. By H. HÜBNER (*Deut. Chem. Ges. Ber.*, x, 2165).—Succinic chloride and benzanilide, when heated together, give rise to a base containing no oxygen; similarly acetanilide forms a base, $C_{29}H_{28}N_4$, readily crystallisable, melting at 132—133°, diacid, the hydrochloride being $C_{29}H_{28}N_4.2HCl$, and the nitrate $C_{29}H_{28}N_4.2HNO_3$: both these salts are crystallisable. It is probable that these are special cases of a general reaction, for acetyl chloride also forms crystallisable products with acetanilide and benzanilide. C. R. A. W.

Ferrocyanides of the Amine Bases. By E. FISCHER (*Liebig's Annalen*, cxc, 184—187).—Acid solutions of amine salts give, with potassic ferrocyanide, difficultly soluble acid salts of the general formula $R_2H_4FeCy_6$; those of the ammonium bases are the most insoluble, and those of the tertiary, secondary, and primary amines, differ in their degree of solubility, the acid ferrocyanides of the primary amines being the most soluble. This difference in the solubility of these salts affords a means of separating these bases, since they are decomposed by alkalis, with formation of an alkaline ferrocyanide and the free base, which may be removed by distillation. In case of an ammonium base, the insoluble acid ferrocyanide, suspended in water, is treated with cupric sulphate, the solution filtered, and the excess of copper sulphate removed from the filtrate by baryta-water: after the excess of the latter has been precipitated by carbon dioxide, the filtrate yields on evaporation the carbonate of the ammonium base.

Aniline ferrocyanide, obtained by precipitation of an acid solution of an aniline salt with potassic ferrocyanide, separates out from concentrated solutions in colourless prismatic crystals, easily soluble in hot water, and crystallising out on cooling.

Dimethyl-aniline ferrocyanide, $[C_6H_5N(CH_3)_2]_2H_4FeC_6N_6$, is obtained in a similar manner as a difficultly soluble precipitate, crystallising from hot aqueous solutions in colourless plates which, like all these salts, become blue on exposure to the air, owing to the formation of Prussian blue. The amines of the fatty series differ from those of the aromatic series, the tertiary amines being the first to form difficultly soluble ferrocyanides, and therefore can be separated from a mixture containing at the same time primary and secondary bases.

Triethylamine ferrocyanide, $[(C_2H_5)_3N]_2H_4FeC_6N_6$, forms colourless, shining plates.

The acid ferrocyanides of the ammonium bases, both of the fatty and aromatic series, are precipitated from strongly acid solutions of their iodides, chlorides, and sulphates, by potassic ferrocyanide.

Tetramethylammonium ferrocyanide separates from hot water in crystals, having the composition $[(CH_3)_4N]_2H_4FeC_6N_6 + 2H_2O$.

Dimethylethylphenylammonium ferrocyanide has the composition $[C_6H_5(CH_3)_2C_2H_5.N]_3H_5.Fe_2(CN)_{\cdot 2} + 2H_2O$.

Diethylphenylazonium ferrocyanide is a difficultly soluble compound, and has the composition $[C_6H_5N_2H_2(C_2H_5)_2]_3H_5Fe_2C_{12}N_{12} + 2H_2O$.

P. P. B.

Addition of Hydrogen Cyanide to Benzoylanilide. By C. O. Cech (*Deut. Chem. Ges. Ber.*, xi, 247—249).—When a solution of potassium cyanide is added to a mixture of benzaldehyde and aniline (or aniline hydrochloride) dissolved in alcohol, the liquid at once turns milky, evolves hydrogen cyanide, and deposits a heavy brown oil, which afterwards solidifies. The product of the reaction is soluble in alcohol, ether, and carbon bisulphide, crystallises in yellowish or white silky needles, sublimes in delicate white needles, and distils with water. It is insoluble in soda-ley and in dilute acids, but is decomposed by the latter when hot. It melts at 82°. The composition of the body agrees with the formula $C_{14}H_{12}N_2 = C_{13}H_{11}N + CHN$, and its formation is represented by the equation $C_7H_6O + C_6H_7N + CHN - H_2O = C_{14}H_{12}N_2$.

A body, of the formula $C_{13}H_{11}N$, was obtained by Laurent and Gerhardt by the action of benzaldehyde on aniline, and was called by them "benzoylanilide" (*Compt. rend.*, 1850, 117). The same body was afterwards examined by H. Schiff, who doubled its formula and regarded it as ditoluylene-diphenyl-diamine, $N_2(C_7H_6)_2(C_6H_5)_2$ (*Liebig's Annalen*, cxxxvi, 343).

The author finds that benzoylanilide obtained by the reaction of benzaldehyde with aniline combines directly with hydrogen cyanide, to form a compound identical with that described above, which may, therefore, be regarded as benzoylanilide hydrocyanide. Moreover, the latter is resolved by heating with water or hydrochloric acid into hydrogen cyanide and benzoylanilide.

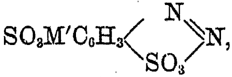
The foregoing results show that benzaldehyde differs from chloral in its behaviour with aniline and potassium cyanide (see this *Journal*, 1876, i, 376, ii, 66; 1877, i, 67). The author is examining the behaviour of other aldehydes under similar conditions. J. R.

Substituted Thiamides. By H. LEO (*Deut. Chem. Ges. Ber.*, x, 2133).—When sulphuretted hydrogen acts on benzanilide chloride, $C_6H_5.CCl.NC_6H_5$, hydrochloric acid is evolved, and *thiobenzanilide*, $C_{13}H_{11}NS$, is formed; after crystallisation from alcohol and ether, this compound melts at 95—97°. Similarly *thiobenzotoluide*, melting at 128·5—129·5°, is obtained from benzotoluide chloride; and *thioacetanilide*, melting at 74·5—76° from acetanilide chloride. The chlorides from which these thiamides are formed are readily obtained by acting on benzotoluide and acetanilide with phosphorus pentachloride. These thiamides appear to be weak acids, being soluble in aqueous soda solution and precipitable from these solutions by acids; in this way they are readily separable from ordinary aciamides.

Iodine has no action on thiobenzanilide, nor can it be saponified by aqueous hydrochloric acid; alcoholic potash at 150° regenerates benzanilide: on fusing it with aniline hydrochloride, *benzenyl-diphenyl-amidine* is formed: when it is heated alone to above 360°, sulphuretted hydrogen is evolved, and a yellow-brown distillate is obtained from which crystals separate, melting at 111·5—112·5°, and containing $C_{27}H_{20}N_2S_2$. Ethyl sulphydrate has no action on benzanilide chloride.

C. R. A. W.

Derivatives of Benzenemetadisulphonic Acid. By Dr. G. HEINZELMANN (*Liebig's Annalen*, cxc, 222—229).—(1.) (α) *Nitro-benzenedisulphonic Acid.*—The basic barium salt of this acid, formed by the action of barium hydrate on the neutral salt, crystallises in slightly yellow, easily soluble needles, having the composition $C_6H_3\left\{\begin{matrix}NO_2\\(SO_3)_2Ba.\end{matrix}\right.BaH_2O_2.15H_2O$. The basic lead salt is produced by treating a solution of the neutral salt with lead acetate; it crystallises out on the sides of the vessel in hemispherical masses formed by union of needles; is insoluble in cold water, and difficultly soluble in hot water. It has the composition $C_6H_5\left\{\begin{matrix}NO_2\\(SO_3)_2Pb\end{matrix}\right.PbO + 2\tfrac{1}{2}H_2O$.

(2.) *Diazo-compounds of* (α) *Amidobenzene-disulphonic Acid.*—The neutral salts of amidobenzene-disulphonic acid, when treated with nitrous acid, are converted into the diazo-compounds, and the author has shown (*Deut. Chem. Ges. Ber.*, ix, 1534) that they have the constitution  $SO_3M'C_6H_3\left<\begin{matrix}N\\SO_3\end{matrix}\right>N$, and not that attributed to them in a former publication (*Ann. Chem. Pharm.*, clxxviii, 173). Barium (α) amidobenzenedisulphonate yields, on heating its aqueous solution with nitrous acid, a gelatinous mass, from which a body crystallising in prisms is obtained; it is difficultly soluble in cold, more easily in hot water. Analysis shows its composition to be—

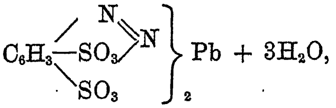
$$C_6H_3\left\{\begin{matrix}N{=}N{-}HN\\(SO_3)_2BaBa(SO_3)_2\end{matrix}\right\}C_6H_3 + 7H_2O.$$

Heated with water to 80—90°, it gives off nitrogen.

A lead salt having the composition—

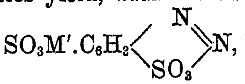
$$C_6H_3\left\{\begin{matrix}N{=}N{-}HN\\(SO_3)_2Pb.Pb(SO_3)_2\end{matrix}\right\}C_6H_3 + 4H_2O,$$

may be obtained in a similar manner. It crystallises in slender needles, and is difficultly soluble in water. If nitrous acid gas be passed into the solution for some time, and alcohol added, a salt crystallises out in needles having the composition—



which is identical with one already described by the author (*op. cit.*).

(3.) (β) *Amidobenzenedisulphonic Acid.*—The neutral potassium salt, $C_6H_3(NH_2)(SO_3K_2)_2.H_2O$, crystallises in quadrangular and hexagonal columns, and is easily soluble in water. The acid barium salt, $(C_6H_3.NH_2.SO_3H.SO_3)_2Ba.H_2O$, has been described by the author (*loc. cit.*) as having two molecules of water of crystallisation.

The neutral β-amidobenzenedisulphonates yield, with nitrous acid, diazo-compounds having the composition , but do not form any mediate compounds like those obtained from the (α) amidobenzenedisulphonic acid.

(4.) (β) *Bromobenzenedisulphonic Acid.*—The salts of this acid are obtained by treating the salts of β-diazobenzenedisulphonic acid with hydrobromic acid.

The potassium salt, $C_6H_3Br(SO_3K)_2H_2O$, crystallises in hard, white, wart-like masses.

(β) *Bromobenzenedisulphochloride*, $C_6H_3Br(SO_2Cl)_2$, is formed by the action of phosphorous chloride on the potassium salt. It crystallises from ether in thin shining plates united to warty or scaly masses, and melts at 103°. When the chloride is treated with ammonia, the amide is formed, having the composition $C_6H_3Br(SO_2NH_2)_2$. It is difficultly soluble in cold, easily in hot water, crystallising from the latter solution in white needles which melt at 239°. P. P. B.

Xylenesulphonic Acids and Xylenols. By O. JACOBSEN (*Deut. Chem. Ges. Ber.*, xi, 17—29).—*Metaxylenesulphonic Acid*, $C_8H_9SO_3.H = C_6.CH_3.H.CH_3.SO_3H.H_2$.—This acid was prepared from the amido-compound melting at 137°; it usually crystallises in long flat plates containing two molecules of water. Its constitution was determined by distillation with potassium cyanide and digestion with hydrochloric acid, which converted it into xylic acid, melting at 125°. The *barium* salt, $(C_8H_9SO_3)_2Ba$, prepared by cooling a saturated boiling solution, separates in small rhombic, anhydrous plates, or, if obtained by the slow evaporation of a more dilute solution, in large hemispherical groups of rhombic plates. The *sodium* salt is very soluble in water, and separates from its aqueous solution in small anhydrous scales. It is less soluble in alcohol, and crystallises from its alcoholic solution in large glittering plates. The *zinc* salt, $(C_8H_9SO_3)_2Zn + 9Aq$, forms easily soluble star-shaped groups of needles, or occasionally long rhombic prisms. The *copper* salt, $(C_8H_9SO_3)_2Cu + 6Aq$, crystallises easily in large, clear, brown, rhombic tables. The *sulphochloride*,

$C_8H_9SO_2Cl$, melts at 34°, and solidifies to a crystalline mass. With ammonia it yields the *amido-compound*, melting at 137°.

Metaxylenesulphonic acid, $C_8H_9SO_3H = C_6.CH_3.SO_3H.CH_3.H_3$, was obtained from the corresponding amido-compound melting at 95—96°, but could not be crystallised. By the successive action of potassium cyanide and hydrochloric acid, it is converted into a new acid isomeric with xylic acid, and melting at 100°. The salts of the second sulphonic acid are more readily soluble in water than those of the previous acid, and crystallise with less facility. The *barium* salt forms microscopic star-like groups of anhydrous crystals. The *potassium* salt separates in small glittering needles from a concentrated aqueous solution. The copper salt crystallises in brown needles containing water. The *sulphochloride* forms an oily liquid, which does not solidify at 0°, and is converted by treatment with ammonia into the corresponding amido-compound, $C_8H_9SO_2NH_2$, melting at 95—96°. The amide, $C_8H_9SO_2NH_2$, melting at 123°, described by Wittig and Poste, does not appear to exist. (Iles and Ira Remsen thought the higher melting amide probably had the constitution 1 : 2 : 3 (this *Journal*, 1877, ii, 776), and the other the constitution (1 : 3 : 4)).

Paraxylenesulphonic acid, $C_8H_9SO_3H$, crystallises usually in very large flat prisms containing two molecules of water. Its difficultly soluble barium salt, and the finely crystalline sodium salt have been already described (this *Journal*, 1877, ii, 600). The potassium salt, $C_8H_9SO_3K + H_2O$, forms fine groups of flat needles; the copper salt, $(C_8H_9SO_3)_2Cu + 8H_2O$, forms large clear-blue triclinic prisms, and the zinc salt, $(C_8H_9SO_3)_2Zn + 10H_2O$, long needles. The *sulphochloride*, $C_8H_0SO_2Cl$, crystallises in large flat prisms, which melt at 24—26°. The amide, $C_8H_9SO_2NH_3$, melts at 147—148°, is readily soluble in alcohol, but with difficulty in hot water, and crystallises in splendid long needles. *Paraxylensulphinic acid*, $C_3H_9SO_2H$, is a crystalline body melting at 84—85°, and easily soluble in alcohol and ether, but with difficulty soluble in water.

Orthoxylenesulphonic acid, $C_8H_9SO_3H = C_6.CH_3.CH_3.H.SO_3H.H_2$, crystallises in long flat prisms or rectangular tables. Its principal derivatives have been already described (*Chem. Soc. Jour.*, 1877, ii, 601).

Metaxylenol, $C_8H_9OH = (1 : 3 : 4)$, is a colourless, oily liquid, with a strong phenol odour, and refracts light strongly. Its sp. gr. at 0° is 1·0362, and it boils constantly at 211·5° (bar. 766 mm.). It is freely miscible with ether and alcohol, but very slightly soluble in water. Its aqueous solution gives a fine pure blue colour with ferric chloride, and the alcoholic solution a splendid dark-green coloration. Its sodium compound, C_8H_9ONa, is soluble in water and in a concentrated solution of sodium hydrate. *Monobromometaxylenol*, C_8H_8BrOH, is a colourless oily liquid; *dibromometaxylenol* forms long delicate colourless crystals, melting at 73°; and *tribromometaxylenol* crystallises from boiling alcohol in long colourless needles, melting at 179°. When treated with sulphuric acid, metaxylenol forms two sulphonic acids; these yield barium salts which can be separated from each other by fractional crystallisation. The *barium* salt of one of these acids crystallises in rhombic plates or rectangular tables, both of which are anhydrous. It is soluble with difficulty in cold water, but, with great care, in hot water. The potassium salt forms fine groups of anhydrous scales, soluble with difficulty in cold water, and the sodium salt crystallises in large anhydrous tables. The *barium* salt of the other sulphonic acid forms microscopic needles, more soluble in cold water than the former compound. The corresponding sodium salt crystallises from a very concentrated solution in a mass of scales containing four molecules of water.

The *acetyl* derivative, $C_8H_9.OC_2H_3O$, is a colourless liquid, boiling at 226°, and *methyl metaxylenate*, $C_8H_9.OCH_3$, is a colourless liquid boiling at 192°, and having a feeble aromatic odour.

Metaxylenol, (1 : 2 : 3), forms glittering crystals, which melt at 74·5°, and boil at 211—212°. It yields a tribromo-derivative which crystallises from hot alcohol in long yellow needles melting at 175°. With concentrated sulphuric acid it yields two isomeric sulphonic acids: the barium salt of only one of these is crystalline.

Paraxylenol is a crystalline body resembling phenol. It melts at 74·6° and boils at 211·5° (bar. 762). Its aqueous solution is not coloured by ferric chloride. The *sodium* derivative, $C_8H_8.ONa$, forms white crystalline plates, which dissolve slowly in concentrated solution of sodium hydrate. *Monobromoparaxylenol*, $C_8H_8Br.OH$, forms a colourless crystalline mass, melting at 87°. *Tribromoparaxylenol*, $C_8H_6Br_3.OH$, crystallises from hot alcohol in long needles of an intense golden-yellow colour, and melting at 175°. *Paraxylenolsulphonic acid*, $C_8H_8.OH.HSO_3$, is obtained by dissolving paraxylenol in warm sulphuric acid. It crystallises in small plates containing water. Its *barium* salt forms masses of microscopic anhydrous needles, and its *sodium* salt crystallises in fine large rhombic deliquescent tables.

The *acetyl* derivative, $C_8H_9.OC_2H_3O$, is a colourless liquid with a faint odour, boiling at 237° (bar. 768 mm.), and having a sp. gr. of 1·0264 at 15°. *Methyl paraxylenate*, $C_8H_9.OCH_3$, is a colourless oily liquid boiling at 194° (bar. 772 mm.).

Orthoxylenol, (1 : 2 : 4), crystallises from its aqueous solution in very long needles, and from its solution in dilute alcohol in rhombic octahedra. It melts at 61°, and boils at 225° (bar. 757 mm.). The *sodium* derivative, $C_8H_9.ONa$, dissolves with great difficulty in an aqueous solution of caustic soda, and crystallises in masses of glittering needles. *Tribromorthoxylenol*, $C_8H_6Br_3.OH$, crystallises from hot alcohol in delicate snow-white crystals, melting at 169°. The *barium* salt of the sulphonic acid is soluble with difficulty in cold water, and the *sodium* salt crystallises in anhydrous long flat prisms. With ferric chloride the salts of the orthoxylenolsulphonic acid gave an intense violet colour.

E. N.

Oxidation of Xylene-sulphonic Acids. By M. W. ILES and IRA REMSEN (*Deut. Chem. Ges. Ber.*, xi, 229—232). In former papers the authors have described the preparation of three amides of xylenesulphonic acid, two of which have since been examined by Jacobsen (*Deut. Chem. Ges. Ber.*, x, 1015). The third amide, which has not yet been obtained pure, proves to be a derivative of para-xylene. It yields, by oxidation with sulphuric acid and potassium bichromate, an acid which crystallises in long silky needles melting at 267°, and dissolving freely in boiling water and in alcohol. The new acid yields paratoluic acid when heated with strong hydrochloric acid in sealed tubes, and is therefore regarded as *sulphamido-paratoluic acid*, $C_6H_3.CH_3 : SO_2NH_2 : COOH = 1 : 2 : 4$. The following salts of this acid have been prepared. They all crystallise in needles and dissolve easily in water:—

Barium salt, $(C_6H_3.CH_3.SO_2NH_2COO)_2Ba + 2H_2O$.
Calcium salt, $(C_6H_3.CH_3.SO_2NH_2\,COO)_2Ca + 4H_2O$.
Manganese salt, $(C_6H_3.CH_3.SO_2NH_2.COO)_2Mn + 5H_2O$.

Further examination of *sulphamido-metatoluic acid* has shown that it melts at 248°, and not at 235° as previously stated. It crystallises from alcohol, in which it is easily soluble, in peculiar curved prisms. Its sodium, copper, cobalt, calcium, silver, and barium salts all crystallise in needles and dissolve easily in water. J. R.

On Pseudocumenol and the Constitution of Pseudocumenesulphonic Acid, Durene, &c. By A. REUTER (*Deut. Chem. Ges. Ber.*, xi, 29—32).—*Pseudocumenol*, $C_9H_{11}.OH$, is a white crystalline body, melting at 69° and boiling at 240°; it is nearly insoluble in cold water, but easily soluble in alcohol and ether. Its aqueous solution does not produce any coloration with ferric chloride.

Monobromopseudocumenol forms long colourless needles, melting at 32° and boiling with decomposition at 250°.

Dibromopseudocumenol crystallises from hot alcohol in large colourless needles, melting at 149—150°.

Pseudocumenesulphonic acid forms small glittering needles. Its *barium* salt is soluble with difficulty and forms glittering plates. The *potassium* and *zinc* salts crystallise in large long plates.

Oxyxylylic acid, $C_6H_2(CH_3)_2(OH).COOH$. When pseudocumenol is fused with potash, and the product is decomposed by hydrochloric acid, and extracted with ether, it yields an *oxyxylylic acid*, which, when pure, crystallises from a hot aqueous solution in groups of needles or small rhombic prisms. The crystals are very easily soluble in alcohol and ether. It melts at 195° and readily sublimes. Its *barium* salt forms small crystals and the *calcium* salt an amorphous mass. The calcium salt on being distilled yields metaxylenol (1 : 3 : 4), agreeing with Jacobsen's description (this *Journal*, p. 411). From this basis therefore the constitution of the bodies described above must be as follows:—Oxyxylylic acid, $(CH_3{:}CH_3{:}OH{:}COOH = 1 : 3 : 4 : 6)$; Pseudocumenol, $(CH_3{:}CH_3{:}OH{:}CH_3 = 1 : 3 : 4 : 6)$; Pseudocumenolsulphonic acid, $(CH_3{:}CH_3{:}SO_3H{:}CH_3 = 1 : 3 : 4 : 6)$.

When a mixture of potassium *pseudocumenesulphonate* and sodium formate are fused, durylic acid or an isomeride is formed. This new acid is only slightly soluble in hot water, still less so in cold water, but easily soluble in alcohol or ether and moderately soluble in benzene. It crystallises from alcohol in compact glittering prisms and from benzene in long needles. It melts at 149° and sublimes in long delicate needles. It is therefore identical with durylic acid, $C_{10}H_{12}O_2$. It follows therefore that durene, $C_6H_2(CH_3)_4$, must possess the constitution 1 : 2 : 4 : 6. This therefore confirms the view which Jannasch has adopted as probable (this *Journal*, 1877, ii, 751). E. N.

Derivatives of Pseudocumenesulphonic Acid. By J. Rudloff (*Deut. Chem. Ges. Ber.*, xi, 32).—*Pseudocumolsulphochloride*, $C_9H_{11}.SO_2Cl$, crystallises in large, transparent, monoclinic prisms, melting at 61°.

Pseudocumolsulphinic acid, $C_9H_{11}.SO_2H$, forms long needles, melting at 98°, which, when pure and dry, do not oxidise in the air. Its *sodium* salt crystallises in easily soluble rectangular tables. The *barium* salt forms heavy rhombic tables, soluble in 20 parts of water at a temperature of 7°. The *silver* salt is soluble with difficulty in water.

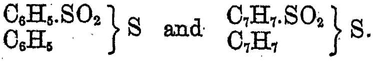
Pseudocumene Sulphydrate, $C_9H_{11}.SH.$, crystallises from alcohol in rectangular plates, melting at 85°. With lead acetate it gives a yellow and with silver nitrate a reddish-yellow precipitate, both of which are insoluble in water and alcohol. With mercuric chloride it gives a compound of the formula, $(C_9H_{11}S)_2Hg$, insoluble in water, but soluble in hot alcohol, from which it crystallises in fine colourless needles.

Pseudocumene Disulphide, $(C_9H_{11})_2S_2$, is obtained by the action of hydrogen sulphide on a hot concentrated alcoholic solution of the sulphinic acid. The disulphide separates out in small crystals, melting at 115°.
E. N.

Formation and Constitution of Benzene- and Paratoluene-Disulpho-dioxides. By C. Pauly and R. Otto (*Deut. Chem. Ges. Ber.*, x, 2181—2185).—The resolution of benzene- and paratoluene-sulphinic acids into the corresponding disulpho-dioxide and sulphonic acid respectively, is determined, not only by boiling them with water and by leaving them over dehydrating agents, as the authors have previously shown, but also by contact with HCl gas. This explains the apparently spontaneous passage of sulphinic acids, as ordinarily prepared by decomposition of their sodium salts with hydrochloric acid, into a disulpho-dioxide and sulphonic acid. By heating an alcoholic solution of benzene disulpho-dioxide with zinc-dust it is completely decomposed into zinc sulphinate and mercaptide, according to the equation—

$$2C_{12}H_{10}S_2O_2 + 2Zn = Zn(C_6H_5.SO_2)_2 + Zn(C_6H_5.S)_2.$$

The toluene compound is similarly decomposed. Hence these compounds must be regarded as ether-derivatives of corresponding thiosulphonic acids, and as having the constitution represented by the formulæ—



$$\left.\begin{matrix} C_6H_5.SO_2 \\ C_6H_5 \end{matrix}\right\} S \quad \text{and} \quad \left.\begin{matrix} C_7H_7.SO_2 \\ C_7H_7 \end{matrix}\right\} S.$$

By boiling the disulpho-dioxides with the aqueous alkalis, they are decomposed, with formation of sulphonic and sulphinic acids, disulphides, and sulphydrates in small quantity, according to the several equations—

1. $(C_6H_5.SO_2).C_6H_5.S. + H_2O = (C_6H_5.SO_2).H.O + C_6H_5.S.H.$
2. $(C_6H_5.SO_2).C_6H_5.S. + C_6H_5.SH = C_6H_5.SO_2H + (C_6H_5)_2S_2.$
3. $2(C_6H_5)_2S_2 + 2H_2O = 3(C_6H_5.SH) + C_6H_5.SO_2H.$

In support of equation 2, the authors cite the reaction which they have observed between benzene disulpho-dioxide and zinc phenylmercaptide. On mixing cold alcoholic solutions of these bodies, benzene disulphide and zinc benzenesulphinate are formed, thus:—

$$2[(C_6H_5.SO_2).S.C_6H_5] + (C_6H_5)_2S_2Zn = 2(C_6H_5.SO_2)_2Zn + 2(C_6H_5)_2S_2.$$

This observation also bears out the authors' view of the constitution of the disulpho-dioxides. C. F. C.

Aromatic Sulphones. By A. Michael and A. Adair (*Deut. Chem. Ges. Ber.*, xi, 116—121).—It has already been shown (*Deut. Chem. Ges. Ber.*, x, 583; this *Journal*, 1877, ii, 612) that the two naphthylphenyl sulphones prepared by the action of phosphoric anhydride (1) on benzene-sulphonic acid and naphthalene, (2) on β-naphthalene-sulphonic acid and benzene are identical. Similarly it has been found that the phenyl-tolyl sulphones prepared in the same manner from (1) benzene-sulphonic acid and toluene, (2) from paratoluene-sulphonic acid and benzene, are also identical.

Phenyltolyl sulphone, $C_{13}H_{12}SO_2$, crystallises from hot water in fine prisms, melting at 124·5°; it is soluble in alcohol, benzene, and glacial acetic acid in the cold, more easily when heated.

The identity of the product of the two above-named reactions tends to show that sulphur in the sulphonic acids is tetra- or hexatomic, since, according to this supposition, $C_6H_5.SO_2.C_6H_4.CH_3$ is the only possible form, whereas, if sulphur be diatomic, the two isomerides, $C_6H_5S—O—OC_6H_4.CH_3$ and $C_6H_5O—O—SC_6H_4.CH_3$, may exist. The authors regard as improbable the explanation that the identity of the product is brought about by molecular change, since oxygen and sulphur show a great affinity for the benzene and toluene nuclei.

Parasulphobenzidicarbonic acid, $C_6H_5.SO_2.C_6H_4.COOH$.—This compound is obtained by oxidising paratolylphenyl-sulphone by boiling with a dilute aqueous solution of potassium permanganate. It crystallises from its alcoholic solution in small white prisms, and melts above 300°; it is insoluble in water, dissolves, however, easily in hot alcohol, benzene, glacial acetic acid, and nitrobenzene. The lead salt may be obtained as a flocculent white precipitate and the copper salt as a light-blue precipitate. The silver salt is white and flocculent and is very easily acted on by light.

Sulphobenzidicarbonic acid, $SO_2(C_6H_4.COOH)_2$.—This acid is obtained from sulphotoluide in a manner similar to the last-mentioned acid, which is obtained by the action of phosphoric anhydride on paratoluene-sulphonic acid and toluene. The dicarbonic acid crystallises from alcohol in white prisms, which melt above 300°. Alcohol, glacial acetic acid, and benzene do not dissolve it; it is, however, soluble in nitrobenzene.

The barium salt is obtained as a crystalline precipitate, and the silver salt as a white flocculent precipitate.

Phenyltolyl sulphone is acted upon by nascent hydrogen in a manner analogous to sulphobenzide. P. P. B.

Action of Carbon Tetrachloride on Substituted Phenols in Alcoholic Solution. By G. Hasse (*Deut. Chem. Ges. Ber.*, x, 2185—2195).—*Phenols.*—The decomposition of phenol by carbon tetrachloride in presence of alcohol and alkali occurs, as Reimer and Tiemann have shown (*Ber.*, ix, 1285), according to the equation—

$$C_6H_5ONa + CCl_4 + 5NaOH = C_6H_4.ONa.CO.ONa + 3H_2O + 4NaCl,$$

both salicylic and paroxybenzoic acids being formed. The author finds that the latter of these isomerides is formed in the larger quantity.

Orthonitrophenol, when similarly decomposed, yields orthonitrosalicylic acid as the chief product, and a small quantity of a second acid, which appears to be the orthonitroparoxybenzoic (m. p. 186—187°).

Paranitrophenol (m. p. 114°) yields paranitrosalicylic acid (m. p. 228°), in all respects identical with the acid which is obtained as the chief product of the nitration of salicylic acid. No other acid appears to be formed in this reaction.

Parachlorophenol (m. p. 41°) is converted into the corresponding chlorophenolcarbonic acid (m. p. 167—168°). This acid also appears to be the exclusive product of the reaction. By replacing the Cl-atom by hydrogen it is converted into salicylic acid, and may therefore be designated parachlorosalicylic acid.

The author has prepared its barium salt, to which he assigns the formula $\{C_6H_3.OH.Cl.CO.O\}_2Ba.3.H_2O$.

Orthochlorophenol (b. p. 176°) yields a chlorophenolcarbonic acid (m. p. 164—165°), which is probably the ortho-compound. Its crystallised barium salt has the formula $(C_6H_4.ClO_3)_2Ba.6H_2O$.

Salicylic Acid.—By the action of carbon tetrachloride upon salicylic acid at 120—130°, both α- and β-phenoldicarbonic acids are formed (*Ber.*, x, 1570), the former in the larger quantity.

The author also incidentally mentions the formation of a dinitroparachlorosalicylic acid, $C_6H_2.(NO_2)_2Cl.(OH).CO.OH$, by the action of concentrated nitric acid upon parachlorosalicylic acid previously moistened with water. It crystallises in long yellow needles, which melt at 78°. C. F. C.

A New Method of Preparing Acetylamidophenols. By H. N. Morse (*Deut. Chem. Ges. Ber.*, xi, 232).—When ortho- and paranitrophenols are treated with tin and acetic acid in excess the products of the reactions are not amidophenols, as might be expected, but acetylamidophenols, formed thus:—

$$C_6H_4.OH.NH_2 + CH_3.COOH = H_2O + C_6H_4.OH.NH.C_2H_3O.$$

Ortho-acetylamidophenol thus formed is identical with that which Ladenburg obtained by a different reaction (*Deut. Chem. Ges. Ber.*, ix, 1526).

Para-acetylamidophenol crystallises in large prisms very easily soluble in hot water and in alcohol. It melts at 179°. When gently heated with hydrochloric acid, it is resolved into acetic acid and paramidophenol. J. R.

Action of Ammonium Sulphide on Picramide. By L. M. NORTON and J. F. ELLIOTT (*Deut. Chem. Ges. Ber.*, xi, 327—328).—The authors have isolated the red body which was observed by Clemm (*J. pr. Chem.*, 109—158) to be formed as a product of the reaction of the above compounds. It is most conveniently prepared by heating picramide with alcoholic solution of ammonium sulphide at 130°. It crystallises from alcohol in long, slender, red needles, which melt at 210°, and the composition of which is expressed by the empirical formula $C_6H_6N_4O_4$. It is a base, and yields the chloride, $C_6H_6N_4O_4.HCl$, which is at once decomposed by water. By the action of acetyl chloride the diacetyl-compound, $C_6H_4(C_2H_3O)_2.N_4O_4$, is obtained, crystallising in slender bright yellow needles (m. p. 245°). For the constitution of the original base the authors propose the formula, $C_6H_2.(NO_2)_2.(NH_2)_2$, and designate it *β-dinitrophenylendiamine.* It resists the action of powerful reducing agents. C. F. C.

Triatomic Phenols from Beechwood Tar, and the Origin of Coerulignone. By A. W. HOFMANN (*Deut. Chem. Ges. Ber.*, xi, 329—338).—The author's researches establish the presence of a series of trihydric phenols in the acid distillate from beechwood tar, which comes over between 240° and 290°. Of these the higher homologues, $C_8H_{10}O_2$ and $C_{11}H_{16}O_3$, are best known (*Ber.*, viii, 66). The following observations throw much additional light upon the constitution of the compound, $C_{11}H_{16}O_3$. Treatment with acetic anhydride converts it into the monaceto-derivative, $C_{11}H_{15}(C_2H_3O)O_3$, which crystallises from alcohol in colourless prisms (m. p. 87°); on treatment with bromine this yields the dibromo-derivative, $C_{11}H_{13}Br_2.(C_2H_3O)O_3$ (m. p. 102°). A benzoyl-derivative (m. p. 81°) is obtained by the action of benzoyl chloride on the original phenol.

Both the phenol and its aceto-derivative are decomposed by heating with concentrated HCl at 130°, methyl chloride being formed, and also a compound, $C_9H_{12}O_3$, which crystallises in prisms (m. p. 80°), the reaction with the phenol being—

$$C_{11}H_{16}O_3 + 2HCl = C_9H_{12}O_3 + 2CH_3Cl.$$

This is, therefore, regarded by the author as the true phenol, and the constitutional relation of the above derivatives as that represented by the formulæ—

$$C_9H_9(OH)_3,\ C_9H_9(OCH_3)_2(OH),\ \text{and}\ C_9H_9(OCH_3)_2(O.C_2H_3O).$$

Further the formation of dibromine-derivatives of the above compounds renders it probable that the (C_9H_9) group has the constitution, $\{C_6H_2.(C_3H_7)\}'''$.

The dimethyl ether of propylpyrogallic acid—as the original oil is hence regarded—yields on oxidation a quinone, $C_8H_8O_4$, crystallising in yellow needles; and from the latter a hydroquinone, $C_8H_{10}O_4$ (m. p. 160°) may be obtained. The probable constitution and relation of these bodies are the following:—

$$C_6H_2.\begin{cases} OCH_3O \\ OCH_3O \end{cases} \text{and}\ C_6H_2\begin{cases} OCH_3OH \\ OCH_3OH. \end{cases}$$

This view is strengthened by the fact of the formation of a dibromoquinone, $C_6H_6Br_2O_4$, a body crystallising in red needles (m. p. 175°). The quinone and hydroquinone unite to form an intermediate compound crystallising in red needles; the latter further yields, on treatment with benzoyl chloride, a dibenzoyl-derivative,

$$C_6H_2.(OCH_3)_2.(O.C_7H_5O)_2$$

(m. p. 245°); acetyl-derivatives have also been prepared.

By means of its benzoyl-derivative, the author has isolated from the original tar distillate a second body, crystallising in colourless prisms (m. p. 51—52°). The formula of this body, $C_8H_{10}O_3$, has been controlled by the determination of its vapour-density. It is decomposed by concentrated HCl at 100°, with formation of methyl chloride and pyrogallic acid, and is therefore a dimethyl ether of the latter, $C_6H_3.OH.(OCH_3)_2$. It is converted by oxidising agents, into coerulignone, according to the equation, $2.C_8H_{10}O_3 + O_2 = C_{16}H_{16}O_6 + 2H_2O$. The author has effected the synthesis of this compound from pyrogallic acid, through its dimethyl ether. It is remarkable that on substituting the remaining (OH) group in the latter compound by $(O.C_2H_3O)$, the action of oxidising agents on the product results in the formation, not of coerulignone, but of the quinone mentioned above. The cause appears to lie in the removal, with the OH group, of the tendency to condensation, the oxidising action being now confined to one molecule, thus:—

$$C_6H_3\left\{\begin{matrix}(OCH_3)_2\\ O.C_2H_3O\end{matrix}\right. + O_2 = C_6H_2.\left\{\begin{matrix}OCH_3O\\ OCH_3O\end{matrix}\right. + C_2H_3O.OH.$$

This reaction confirms the author's views of the formation and constitution both of the quinone and of coerulignone. C. F. C.

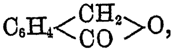
Polythymoquinone. By C. Liebermann (*Deut. Chem. Ges. Ber.*, x, 2177—2179).—The author has investigated and established the polymerisation of thymoquinone when exposed to light; its conversion is proved to be entirely due to the action of this agent.

The resulting modification crystallises from its solution in alcohol, in bright yellow silky needles, which melt at 200—201°, and sublime unchanged at a higher temperature. The attempted determination of its vapour-density, however, in the vapour of sulphur, failed by reason of the substance becoming partially carbonised.

By boiling polythymoquinone with hydriodic acid and amorphous phosphorus, as well as by treating its boiling alcoholic solution with zinc and hydrochloric acid, it is converted into thymohydroquinone.

While these reactions establish the identity of polythymoquinone, its superior stability, as compared with thymoquinone, is evident from the following observations:—It is dissolved unchanged in the cold by concentrated sulphuric acid; it is but slightly attacked, even on prolonged heating, by bromine in presence of water, or of acetic acid, and lastly, water, acetic anhydride, and sulphurous acid solution are without action upon it at 180°. It is dissolved unchanged by fuming nitric acid, a property which appears to be established for the quinone generally. C. F. C.

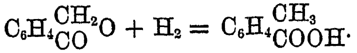
Phthalide (Phthalic Aldehyde) and Meconin. By J. HESSERT (*Deut. Chem. Ges. Ber.*, xi, 237—241).—Continuing his researches on phthalic aldehyde (*Deut. Chem. Ges. Ber.*, x, 1445; *Journ. Chem. Soc.*, xxxiv, 66), the author has arrived at the conclusion that the constitution of this body is represented by the formula—



$$C_6H_4<\substack{CH_2\\CO}>O,$$

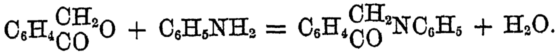
according to which it is the anhydride of *oxymethyl-benzoic acid*, $C_6H_4.CH_2(OH).COOH$, a body described in the former paper as formed by the action of alkalis on phthalic aldehyde. The author proposes the name *phthalide*, instead of phthalic aldehyde.

Phthalide boiled with hydriodic acid and phosphorus yields orthotoluic acid—



$$C_6H_4\substack{CH_2\\CO}O + H_2 = C_6H_4\substack{CH_3\\COOH}.$$

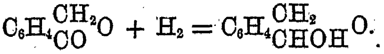
With aniline at 200° phthalide reacts as follows:—



$$C_6H_4\substack{CH_2\\CO}O + C_6H_5NH_2 = C_6H_4\substack{CH_2\\CO}NC_6H_5 + H_2O.$$

The compound thus formed yields by oxidation first *phthalanil*, $C_6H_4(CO)_2NC_6H_5$, and then phthalanilic acid.

Sodium-amalgam acting on phthalide in alkaline solution forms oxymethyl-benzoic acid (see above); but in acid solution the chief product is *hydrophthalide*—

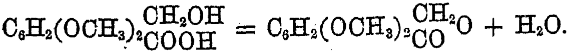


$$C_6H_4\substack{CH_2\\CO}O + H_2 = C_6H_4\substack{CH_2\\CHOH}O.$$

Meconinic Acid.—When meconin is dissolved in baryta-water, and the excess of baryta is removed by means of carbonic acid, the solution leaves on evaporation the barium salt of meconinic acid,

$$[C_6H_2(OCH_3)_2(CH_2OH)COO]_2Ba.$$

This salt is easily soluble in water, and is decomposed by strong acids, the meconinic thereby liberated breaking up into water and meconin, thus:—



$$C_6H_2(OCH_3)_2\substack{CH_2OH\\COOH} = C_6H_2(OCH_3)_2\substack{CH_2\\CO}O + H_2O.$$

J. R.

Ketones of the Aromatic Group. By W. STAEDEL (*Deut. Chem. Ges. Ber.*, x, 1830—1841).—I. *Chloracetylbenzene.*—This compound, whose formation by the action of chlorine on the vapour of acetophenone, was first described by Graebe, has been prepared by the author in large quantities. From its alcoholic solution he has obtained crystals belonging to the rhombic system, and having the axial ratio, $a : b : c = 0{\cdot}9957 : 1 : 0{\cdot}2135$.

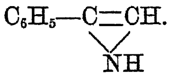
Chloracetylbenzene, $C_6H_5.CO.CH_2Cl$, is insoluble in water, easily soluble in alcohol, ether, and benzene; melts at 58—59° (not at 41°, as given by Graebe), and boils without decomposition at 244—245°. It has an agreeable aromatic odour, but its vapour acts very strongly on the eyes.

II. *Isoindol.*—This compound, produced by the action of aqueous ammonia on chloracetylbenzene, has the same percentage composition as indol. Isoindol is difficultly soluble in all solvents, but may be obtained from its solution in acetic anhydride, in beautiful, thick, tabular crystals, having a pale green tinge, and exhibiting fluorescence; they melt at 194—195°. From its solution in concentrated aqueous hydrochloric acid, it separates in colourless crystals. The constitution of this body, if the condensation takes place in one molecule—which appears probable—may be represented as follows:—

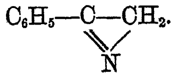
I.

$C_6H_5—C\equiv C—NH_2$.

II.



III.



Formula III is rendered probable by the fact that isoindol is unacted on by acetic acid at 150°, by acetic anhydride at 130—140°, and acetyl chloride at 120°, and ethyl iodide at 100°; moreover, it is not affected by fuming hydrobromic acid, which, according to the researches of Fittig, forms addition-products in cases where carbon-atoms are doubly or triply united. This conclusion is still further strengthened by the fact that isoindol is entirely unchanged by fusion with potassium hydrate.

III. *Nitro-derivatives of Benzophenone.* By H. PRÄTORIUS.—The mixture produced by dissolving benzophenone in fuming nitric acid (sp. gr. 1·8—1·54), warming the solution to about 60°, and then pouring it into cold water, was purified by dissolving it in glacial acetic acid, which deposited a dinitrobenzophenone, $C_{12}H_8(NO_2)_2CO$, in needles melting at 189—190°. The portion more soluble in acetic acid gave by crystallisation from toluene, tabular crystals of a dinitrobenzophenone, melting at 148—149°. By evaporation of the toluene mother-liquors, a mixture of prisms and plates was obtained; the prisms melt at 118°, and are probably those of a dinitrobenzophenone.

In the nitration of benzophenone in the cold, a compound was obtained, crystallising in needles, melting at 127—129°, and corresponding with the so-called dinitrobenzophenone of Linnemann (*Ann. Chem. Pharm.* cxxxiii, 1). This, however, the authors found to be a mixture from which the two dinitrobenzophenones, melting at 189° and 148° respectively, could be isolated by crystallisation from glacial acetic acid. Benzhydrol, on nitration, yields benzophenone and two dinitrobenzophenones melting at 189° and 149°.

IV. *Dioxydiphenylmethane.* By CARL BECK.—This phenol, the preparation of which has already been described (*Deut. Chem. Ges. Ber.*, ix, 562), crystallises from water in yellowish-white, bulky, crystalline masses, and from alcohol in compact monoclinic crystals. It is easily soluble in ether, tolerably so in chloroform, and is insoluble in carbon bisulphide; it melts at 158°, and sublimes at a higher temperature. Potassium hydrate dissolves it easily, and carbonic acid reprecipitates it from this solution; ferric chloride imparts to its solution a yellowish-brown turbidity, which on standing becomes a purple-red. Bromine water produces in its aqueous solution a yellow precipitate.

Various compounds of this phenol are described, *e.g.*, the methyl and ethyl ethers, which are both crystalline bodies. The acetic and benzoic ethers produced by the action of the acid chlorides on the phenol are both solid crystalline bodies, which are easily decomposed by alkalis.

Bromine-water produces in the aqueous solution of this phenol a precipitate of the *tetrabromdioxydiphenylmethane*, $C_{13}H_8Br_4O_2$, crystallising in small, reddish plates, which melt at 225°, and are easily soluble in alcohol and in ether. Bromine acts on the ethereal solution of this phenol to produce a yellow crystalline mass of the unstable compound, *tetrabromdioxydiphenylmethane hydrobromide*, $C_{13}H_9Br_5O_2$, which loses hydrobromic acid on exposure to the air.

The oxidation of the ethylic ether of this phenol, by a solution of chromic acid in glacial acetic acid, yields the ethylic ether of dioxybenzophenone, $CO{=}C_{12}H_8(OC_2H_5)_2$, which melts at 131°, sublimes when more strongly heated, and is less soluble in alcohol than the ether of dioxydiphenylmethane. Dioxydiphenylmethane, when oxidised by fusion with potassium hydrate, yields paraoxybenzoic acid and phenol, which although, as the author points out, not conclusive as to the position of the hydroxyl groups in the aromatic nucleus, shows the formula of this phenol to be $C_6H_4(OH).CH_2.C_6H_4(OH)$.

P. P. B.

Dimethylamidophenylglyoxalic Acid. By W. MICHLER and U. HANHARDT (*Deut. Chem. Ges. Ber.*, x, 2081—2083).—The ethylic ether of dimethylamidodiphenylglyoxalic acid, prepared by the action of one molecule of the chloride of ethyloxalic acid, $COCl.COOC_2H_5$, on two molecules of dimethylaniline, crystallises from an alcoholic solution in yellow scales, which melt at 95°, and decompose on distillation. This substance is soluble in alcohol, ether, carbon bisulphide, benzene, and chloroform, but is insoluble in water.

To obtain the free acid, $(CH_3)_2NC_6H_4.CO.COOH$, the ether is saponified with baryta, and the barium salt converted into lead salt, which is suspended in hot water and decomposed by sulphuretted hydrogen. The acid forms small, yellow, needle-shaped crystals, which melt at 187°, and are soluble in water and alcohol, but less soluble in ether and chloroform.

W. C. W.

Para-iodobenzyl Compounds. By C. F. MABERY and C. L. JACKSON (*Deut. Chem. Ges. Ber.*, xi, 55—58).—*Para-iodobenzyl bromide*, $C_6H_4I.CH_2Br$, formed by the action of bromine on para-iodotoluene at temperatures above 115°, crystallises in white flat needles, having an aromatic odour, and melting at 78·75°. It sublimes in needles, and dissolves in hot alcohol, ether, benzene, and carbon bisulphide, but not in water.

Para-iodobenzyl alcohol, $C_6H_4I.CH_2OH$, produced by boiling the bromide with water, forms white, silky scales of unpleasant odour, melting at 71·75°, and dissolving easily in alcohol, ether, benzene, and carbon bisulphide; sparingly in water.

Para-iodobenzyl cyanide, $C_6H_4I.CH_2CN$, crystallises from alcoholic solutions in white, pearly laminæ, which melt at 50·5°, and resemble the preceding compounds in solubility.

Para-iodoalphatoluic acid, $C_6H_4I.CH_2.COOH$, obtained by heating the nitril at 100° with fuming hydrochloric acid. forms white pointed plates, of agreeable odour, melting at 135°, and subliming at a somewhat higher temperature. By oxidation with chromic acid it is converted into para-iodobenzoic acid. Its *silver salt* crystallises from solution in boiling water in brilliant plates, easily soluble in dilute nitric acid. The *barium* and *calcium salts* form easily soluble white needles. The *zinc* and *magnesium salts* are crystalline, and sparingly soluble. Precipitates are produced by an ammoniacal solution of the acid in solutions of cupric sulphate, lead acetate, mercurous nitrate, aluminium and ferric chlorides, and nickel nitrate.

Para-iodobenzylamines.—The bromide, when heated with alcoholic ammonia, yields a bulky precipitate, which is resolved by crystallisation into the two following bodies:—

1. *Tri-paraiodobenzylamine*, $(C_6H_4I.CH_2)_3N$, the less soluble product, crystallises in white needles, melting at 114·5°, and dissolving easily in ether, benzene, and carbon bisulphide. It forms with platinic chloride yellow needles of the salt, $[(C_6H_4I.CH_2)_3NH]_2PtCl_6$.

2. *Di-paraiodobenzylamine*, $(C_6H_4I.CH_2)_2NH$, the more soluble product, forms white needles, melting at 76°. It forms with hydrochloric acid a salt, crystallising in thick white plates, of very high melting-point, easily soluble in carbon bisulphide and glacial acetic acid. The platinochloride, $[(C_6H_4ICH_2)_2NH_2]_2PtCl_6$, forms pale-yellow crystals.

Para-iodobenzyl thiocyanate, $C_6H_4I.CH_2.SCN$, formed by the action of the bromide on potassium thiòcyanate, crystallises in long white plates of pleasant odour, melting at 40°. It dissolves easily in ether, benzene, carbon bisulphide, and glacial acetic acid; sparingly in alcohol.

J. R.

Action of Iodine on Phenyl-mercurammonium Chloride. By C. RUDOLPH (*Deut. Chem. Ges. Ber.*, xi, 78—82).—When finely-divided iodine is added to an equal number of molecules of phenyl-mercurammonium chloride suspended in alcohol, a reaction takes place resulting in the formation of mercuric iodide, which is deposited in crystals. The filtered liquid, after being freed from mercury in solution by means of hydrogen sulphide, contains the hydrochlorides and hydriodides of mono- and di- iodaniline. The bases liberated from these salts by soda were separated by the process employed by Mills and by Griess to separate mono- and di- chloraniline.

Di- iodaniline crystallises in colourless needles or prisms, which melt at 96°. It dissolves easily in ether, acetone, chloroform, carbon bisulphide, and boiling alcohol, and sparingly in cold alcohol and in boiling water. Its salts are decomposed by water at the ordinary temperature.

The *hydrochloride*, $C_6H_3I_2.NH_2.HCl$, crystallises in colourless brilliant laminæ or needles.

The *platinochloride* $(C_6H_5I_2N.HCl)_2PtCl_4$, forms glistening yellow laminæ.

The *nitrate* crystallises in delicate colourless needles.

Di-iodobenzanilide, $C_6H_3I_2.NH(C_7H_5O)$, obtained by mixing ethereal solutions of di- iodaniline and benzoyl chloride, crystallises in needles, which melt at 181°.

Di-iodaniline, when treated with nitrous acid in alcohol, is converted into meta-di-iodobenzene, a body previously described by Körner. J. R.

Derivatives of Paroxybenzaldehyde. By H. HERZFELD (third Communication, *Deut. Chem. Ges. Ber.*, x, 2196—2199).—Paroxybenzaldehyde unites with paratoluidine, with elimination of water, according to the equation:—

$$C_7H_6O_2 + C_7H_9N = C_{14}N_{13}NO + H_2O.$$

The product of the reaction is an orange-coloured body, which crystallises from its solution in alcohol, in four-sided plates, melting at 213°. The inverse reaction is determined by boiling the compound with dilute acids or alkalis. By passing chlorine gas over the dry paroxybenzaldehyde, chloroparoxybenzaldehyde, $C_6H_3Cl.OH.COH$, is formed, in theoretical quantity. This compound crystallises in long silky needles, which melt at 148—149°, and are freely soluble in water, alcohol, and ether. It forms salts with the alkalis, which crystallise in long needles, and are soluble in water. It absorbs ammonia in the proportion of 1 : 2 molecules, and differs in this respect from paroxybenzaldehyde, 1 molecule of which unites with 1 molecule of NH_3. The compound thus formed crystallises from absolute alcohol in beautiful needles. The aqueous solutions of paroxybenzaldehyde and of its chlorine compound give a violet reaction with ferric chloride.

The corresponding bromine compound, $C_6H_3Br.OH.COH$ (m.p. 179°), is formed when the dilute alcoholic solution of paroxybenzaldehyde is allowed to absorb bromine vapour. It resembles, in all respects, both the latter compound and its chlorine-derivative, with the exception that its aqueous solution is not coloured by ferric chloride.

The iodine compound, $C_6H_3I.OH.COH$ (m.p. 198°), is formed by heating the dilute alcoholic solution of paroxybenzaldehyde with iodine for some hours. By the action of potassium hydrate at a high temperature (160—170°) upon this body, it is converted into protocatechuic acid. C. F. C.

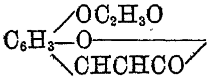
Resorcin Dialdehyde, Resorcyl Aldehyde, and Certain of their Derivatives. By FERD. TIEMANN and LEO. LEWY (*Deut. Chem. Ges. Ber.*, x, 2210—2221).—The authors have extended the investigation of the action of chloroform upon the phenols to resorcin, as a type of the diatomic phenols. Special precautions are required in carrying out these reactions, in consequence of the strong tendency of the dihydroxylbenzenes to form condensation-products with their aldehyde-derivatives.

Resorcin dialdehyde, $C_6H_2(OH)_2(COH)_2$, crystallises from its solution in hot water in long needles, which melt at 127°. It is a stable body, and may be boiled with solutions of the alkalis, in which it is soluble, without undergoing any change. It dissolves in concentrated sulphuric acid, and is precipitated unchanged on the addition of water. Its aqueous solution gives a red-brown reaction with ferric chloride. It is converted into the corresponding dicarbonic acid by fusion with potassium hydrate.

Resorcyl aldehyde, $C_6H_3(OH)_2.COH$, is formed simultaneously with the preceding compound by the action of chloroform (at 62°) on the solution of resorcin in caustic soda. It is obtained in the form of needles, which melt at 134—135°. It is an unstable body, passing into a red amorphous powder, by long exposure to a moist atmosphere.

Diethylresorcyl aldehyde, $C_6H_3(OC_2.H_5)_2COH$, is easily formed by the action of ethyl iodide (2 molecules) and potash (2 molecules) upon resorcin (1 molecule). It crystallises in shining plates (m.p. 71—72°), which are easily soluble in alcohol and ether. It is readily converted into the corresponding acid by oxidation with potassium permanganate in presence of water. The acid is separated in the form of small needles, which melt at 99°. It forms well crystallised salts with barium and calcium.

With the view to elucidate more completely the constitution of resorcyl aldehyde, the authors have subjected this body to the action of a mixture of acetic anhydride and sodium acetate, by which the aromatic aldehydes generally are converted into condensation-products containing the acrylic acid group, CH=CH—CO. The product of the reaction is an indifferent body, crystallising in large prisms (m.p. 140°), of the composition, $C_{11}H_8O_4$, which appears to be acetoxycoumarin.



$$C_6H_3\begin{array}{l}\diagup OC_2H_3O\\ -O\text{————}\diagup\\ \diagdown CHCHCO\end{array}$$

This compound may be distilled unchanged. Its aqueous solution exhibits a magnificent blue fluorescence.

From the formation of this body from resorcyl aldehyde, it is inferred that the COH-group occupies the ortho-position in relation to one at least of the OH-groups.

Acetoxycoumarin is saponified by dilute potash with formation of β-umbelliferone (oxycoumarin); it is converted by the concentrated alkali into resorcin. These synthetic products, whilst closely resembling the acetumbelliferone and umbelliferone which have been prepared by Hlasiwetz and Kachler, cannot yet be regarded as identical therewith: hence the authors distinguish them by the prefix β. They conclude by applying the results of this research to the discussion of the constitutional relation of coumarin, umbelliferone, and aesculitin.

C. F. C.

Synthesis of Oxyketones. By O. DOEBNER (*Deut. Chem. Ges. Ber.*, x, 1968).—The introduction of an acid radicle into the hydroxyl-group of phenol gives rise to a body which is capable of reacting further with an acid chloride to form the ether of an oxyketone. Thus, for instance, the introduction of the benzoyl-radicle into phenol produces phenyl benzoate, and this substance reacts with benzoyl chloride and zinc chloride to form benzoyl-phenol benzoate. The author is experimenting with other bodies with the object of ascertaining whether the reaction is a general one. J. R.

Pinacones and Pinacolins. By W. THÖRNER and T. ZINCKE (*Deut. Chem. Ges. Ber.*, xi, 65—71).—In a former paper (*Deut. Chem. Ges. Ber.*, x, 1473) the authors described a pinacolin formed by the action of dehydrating agents on benzopinacone. They have since found that the same body is produced by heating benzophenone in alcoholic solution with zinc and hydrochloric acid. The product thus obtained, however, is under some conditions, a mixture of two isomeric bodies distinguished as α- and β-pinacolins. At the same time there is formed a large quantity of benzopinacone, whence it appears that pinacones are intermediate products in the direct conversion of ketones into pinacolins.

β-Benzopinacolin $(C_6H_5)_3C.CO.C_6H_5$, melts at 178—179°. It yields by oxidation benzoic acid and triphenylcarbinol, $(C_6H_5)_3C.OH$, but no triphenylacetic acid, and therefore differs in its behaviour from the pinacolins of the fatty series. When heated to 300° with soda-lime, it yields benzoic acid and *triphenylmethane*:

$$(C_6H_5)_3C.CO.C_6H_5 + NaOH = (C_6H_5)_3CH + C_6H_5.COONa.$$

By reduction with hydriodic acid and phosphorus, β-benzopinacolin yields a hydrocarbon, $C_{26}H_{20}$, presumably tetraphenylethane or triphenylbenzylmethane, $(C_6H_5)_3C—CH_2—C_6H_5$. This hydrocarbon is soluble in benzene, chloroform, carbon bisulphide, hot alcohol, and acetic acid, and sparingly in ether, and crystallises from benzene in brilliant rhombic tables, which speedily turn opaque and fall to powder in the air. It crystallises from alcohol in beautiful long white prisms, which melt at 205—206°, and sublime in small needles at a higher temperature.

α-Benzopinacolin melts at 158—159°, and is not volatilisable without decomposition. It dissolves easily in chloroform, carbon bisulphide, benzene, toluene, and hot acetic acid. It is converted into β-pinacolin by the action of acetyl or benzoyl chloride at a gentle heat, and of hydrochloric or hydriodic acid at 150—160°, and also by prolonged boiling with zinc and hydrochloric acid. Its constitution has not yet been made out.

β-Tolylphenylpinacolin (*Liebig's Annalen*, clxxxix, 110), when heated to 300° with soda-lime, yields benzoic acid and a hydrocarbon, $C_{21}H_{20}$, probably ditolylphenylmethane, $C_6H_5—CH(C_6H_4—CH_3)_2$. This substance crystallises in small shining prisms, which melt at 55—56°, and dissolve easily in ether, chloroform, carbon bisulphide, and benzene.

J. R.

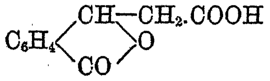
Nitranilic Acid. By R. NIETZKI (*Deut. Chem. Ges. Ber.*, x, 2147).—When nitrous acid is passed into a well-cooled solution of hydroquinone, a crystalline mass of quinhydrone is formed at first by the oxidation of the hydroquinone. Subsequently this disappears, and small golden-yellow crystalline needles separate, readily soluble in water, insoluble in ether. On adding potash to them, they are converted into a sulphur-yellow potassium salt, very sparingly soluble in water, and containing $C_6N_2O_8K_2$ or $C_6(NO_2)_2(OK)_2O_2$: hence the acid formed may be termed *nitranilic acid*, being the dinitro-derivative of a dioxyquinone. The yellow soluble crystals are probably *nitranil*, or tetranitroquinone, decomposed readily in ethereal solution by addition of water, red fumes being evolved and nitranilic acid being formed, crystallisable in golden-yellow prisms, with a bluish dichroism.

Nitranilic acid crystallises in needles a centimeter long, which melt in their water of crystallisation at a little above 100°. When anhydrous, the body decomposes at 170° without melting. It has a strong, acid, ferruginous, astringent taste, not bitter; with most metals it forms well-crystallised salts: thus, with barium chloride, calcium chloride, and silver nitrate, it gives crystalline precipitates.

In addition to nitranilic acid, other nitro-bodies seem to be formed in this reaction, together with much oxalic acid. C. R. A. W.

Action of Dehydrating Agents on Anhydrides. By S. GABRIEL and A. MICHAEL (third communication, *Deut. Chem. Ges. Ber.*, x, 2199—2210).—1. *Derivatives of Phthalylacetic Acid.*—By the action of bromine upon phthalylacetic acid, with careful exclusion of water, phthalylmonobromacetic acid, $C_6H_4(CO)_2CBr.COOH$, is obtained, crystallising in long shining needles (m. p. 232—235°); whereas in presence of water, tribromacetophenone-carbonic acid is formed from the benzoylaceto-carbonic acid, which is produced in the first stage of the reaction (*Ber.*, x, 1555).

By the action of sodium amalgam upon benzoylaceto-carbonic acid (obtained by dissolving phthalylacetic acid in excess of caustic alkali), the authors have previously shown (*Ber.*, x, 1558) that two isomerides of the formula $C_{10}H_8O_4$ are obtained. It appears, however, that the monobasic acid (m. p. 150°) is the sole product of the reduction, and that the bibasic acid described by them is subsequently formed during evaporation. The authors regard the monobasic acid as an anhydride of benzhydrylaceto-carbonic acid, of the form—



+ 1 Aq.

By dissolving this anhydride in baryta-water, and precipitating the excess of the hydrate by carbonic acid, a solution of the barium salt of benzhydrylaceto-carbonic acid is obtained, which with silver nitrate gives a white amorphous precipitate of the corresponding silver salt, $C_6H_4.(COOAg).(CH.OH.CH_2.COOAg)$. On the addition of alcohol to the same solution the barium salt is precipitated as a white amorphous body, which has the composition—

$$\{C_6H_4(.CO.O).(CH.OH.CH_2.CO.O)\}Ba + 1\ Aq.$$

When dried over sulphuric acid at 100°, this salt appears to lose ½ mol. water. Heated to 200° it is converted, with loss of 1 mol. H_2O, into the barium salt of the bibasic acid already mentioned as isomeric with the anhydride $C_{10}H_8O_4$; and from the solution of this salt the acid is separated, on the addition of hydrochloric acid, as a crystalline precipitate. This acid melts at 173—175°, but is at the same time converted into its isomeride.

The conversion of benzhydrylaceto-carbonic into the above dibasic acid also occurs on boiling it with excess of alkali, which appears to exert its dehydrating action on the side group, thus—

$$—CH.OH.CH_2.COOR - H_2O = —CH{=}CH.COOR,$$

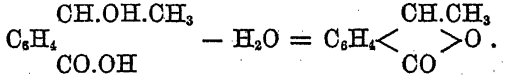
so that the bibasic acid is (ortho) cinnamo-carbonic acid—

$$COOHC_6H_4.CH{=}CH.COOH.$$

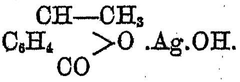
This view is borne out by the observations—(1) that by the action of bromine on the acid in presence of ether, the dibrominated derivative, $C_{10}H_8Br_2O_4$, is obtained, crystallising in needles which melt at 212—213°; (2) that in contact with nascent hydrogen it unites with two atoms of the same to form hydrocinnamo-carbonic acid, $C_{10}H_{10}O_4$, which crystallises in long shining needles, melting at 165—166°. The silver salt of this acid occurs in microscopic needles, which are difficultly soluble in water.

Both bromine and nascent hydrogen are without action on the isomeride.

By the action of sodium amalgam upon acetophenone-carbonic acid in presence of an alkali, a compound is formed, similar in constitution to the anhydride previously mentioned, thus—



$$C_6H_4\begin{matrix}CH.OH.CH_3\\ \\CO.OH\end{matrix} - H_2O = C_6H_4{<}\begin{matrix}CH.CH_3\\ \\CO\end{matrix}{>}O\,.$$



This body is destitute of acid properties, but forms a silver compound, which is represented by the formula $C_6H_4\begin{matrix}CH—CH_3\\ \\CO\end{matrix}{>}O\,.Ag.OH.$ The determination of the vapour-density of the anhydride gave the theoretical result.

By the action of a more powerful reducing agent, viz., a mixture of hydriodic acid and amorphous phosphorus at 180°, acetophenone-carbonic acid is converted into (ortho) ethylbenzoic acid—

$$C_6H_4.(C_2H_5).COOH.$$

Phthalylacetic acid, under the same conditions, also yields this acid.

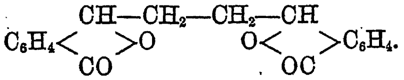
2. *Derivatives of Ethindiphthalyl.*—If (ortho) ethylene-phenylene-ketone-carbonic acid be heated to a temperature somewhat higher than its melting point, it loses 1 mol. water, and is converted into the anhydride $C_{18}H_{12}O_5$. This compound crystallises in long colourless needles, which melt at 228—230°, and are soluble in hot alcohol. The condensation of the molecule of this diortho-compound, in which the substituting groups in each of the benzene nuclei are, in relation to the point of union of the latter, in the ortho-position, generalises recent observations, which go to show that the capacity for this species of condensation is characteristic of ortho-substituted compounds. When heated with hydriodic acid and amorphous phosphorus at 160°, this acid is converted into the compound $C_{18}H_{18}O_4$ (m. p.

196—198°), which appears to be (ortho) ethylenebenzyl-carbonic acid,

$$COOH.C_6H_4.(CH_2)_4.C_6H_4.COOH.$$

By the action of bromine in presence of ether, 2 at. hydrogen are replaced, and dibromethylenebenzoyl-carbonic acid, $C_{18}H_{12}Br_2O_6$, is formed. It crystallises in long white prisms, which melt at 270—272°. Whether the bromine atoms are symmetrically disposed or not remains undecided.

Sodium amalgam in presence of an alkali determines the formation of the anhydride, $C_{18}H_{14}O_4$. This body crystallises in long shining needles which melt at 208—210°. The authors represent its constitution by the formula—



$$\begin{array}{ccc} & CH{-}CH_2{-}CH_2{-}CH & \\ C_6H_4< \quad >O & & O< \quad >C_6H_4. \\ CO & & OC \end{array}$$

C. F. C.

Purpuroxanthin-carbonic Acid and Anthraflavone. By A. ROSENSTIEHL (*Deut. Chem. Ges. Ber.*, x, 2166).—A discussion of the relative bearings of previous researches of the author, and of the somewhat different results obtained by Schunck and Römer, with replies to the criticisms of these chemists. C. R. A. W.

Halogen-derivatives of Alizarin. By T. DIEHL (*Deut. Chem. Ges. Ber.*, xi, 187—192).—*Monochloralizarin*, $C_{14}H_5Cl(OH)_2O_2$.—This substance is formed on passing chlorine into a solution of alizarin in carbon bisulphide containing iodine. It melts at 244—248°, sublimes with partial decomposition in red needles, dissolves very easily in boiling water, and is soluble also in alcohol, ether, and benzene. Its solution in caustic alkalis is reddish-violet; the ammoniacal solution is deep red. As a dye its colour is more inclined to orange than that of alizarin under the same conditions.

Dichloralizarin, $C_{14}H_4Cl_2(OH)_2O_2$, formed by heating alizarin at 90—100° with antimony pentachloride, crystallises in orange-red scales, which dissolve very easily in water and in other solvents. It melts at 208—210°, and sublimes in beautiful orange-red needles. With alum mordant it dyes a fine orange colour; with iron mordant, a brown.

Tetrachloralizarin, $C_{14}H_2Cl_4(OH)_2O_2$, is obtained by heating alizarin at 100° with antimony pentachloride in sealed tubes. It is insoluble in water, but easily soluble in acetic acid, chloroform, benzene, carbon bisulphide, and hot alcohol.

Monobromalizarin, $C_{14}H_5Br(OH)_2O_2$.—A substance having this composition is obtained by heating tribromanthraquinone at 180° with potash. Its melting point lies above 280°. It is uncertain whether this body is identical or only isomeric with Perkin's monobromalizarin.

Dibromalizarin, $C_{14}H_4Br_2(OH)_2O_2$, is formed on heating alizarin with bromine and iodine in the water-bath. It melts at 168—170°, sublimes partially in small brown-red needles, and in other respects resembles dichloralizarin.

Tetrabromalizarin, $C_{14}H_2Br_4(OH)_2O_2$, is produced by heating alizarin at 180° with excess of bromine iodide. It is a crystalline substance, insoluble in alcohol and water, soluble in acetic acid, with brown colour. It melts only at a high temperature, and yields a brown sublimate. J. R.

Chlorine and Bromine-derivatives of Anthracene and Anthraquinone. By T. Diehl (*Deut. Chem. Ges. Ber.*, xi, 173—187).—*Dichloranthracene tetrachloride*, $C_{14}H_8Cl_2.Cl_4$, is formed on passing chlorine over anthracene, at first in the cold, and ultimately at 230°. When pure it crystallises from benzene or toluene in yellowish needles, which melt at 141—145°. It is converted, by heating with alcoholic potash into tetrachloranthracene, melting at 220°.

Hexchloranthracene, $C_{14}H_4Cl_6$, is produced in small quantity by the action of chlorine on anthracene at 260°, or of antimony pentachloride on anthracene at 200° in sealed tubes. It melts at 320—330°, subliming at a lower temperature, and dissolves freely in nitrobenzene ligroïn, and carbon bisulphide. It is not attacked by boiling alcoholic potash or by nitric acid, but is converted into tetrachloranthraquinone by oxidation with chromic acid.

Heptachloranthracene, $C_{14}H_3Cl_7$, formed by heating anthracene at 260° in sealed tubes with antimony pentachloride, sublimes in small needles, which melt at 350°, and dissolve best in ligroïn or nitrobenzene.

Octochloranthracene, $C_{14}H_2Cl_8$, is produced when anthracene is heated at 275—280° with antimony pentachloride. It sublimes in feathery crystals, which do not melt at 350°, and are insoluble in most liquids but sparingly soluble in nitrobenzene and carbon bisulphide.

Hexbromanthracene, $C_{14}H_4Br_6$, is formed by the action of bromine on anthracene containing iodine at 120°. It dissolves in hot benzene toluene, and chloroform, melts at 310—320°, and sublimes in bright-yellow light flocks. It is not affected by alcoholic potash or nitric acid, but is oxidised by chromic acid, yielding tetrabromanthraquinone

Heptabromanthracene, $C_{14}H_3Br_7$, formed by heating dibromanthracene at 200° with bromine and iodine, sublimes without decomposition in yellow needles, which dissolve best in chloroform or carbon bisulphide. It does not melt at 350°, and is not affected by the ordinary reagents.

Octobromanthracene, $C_{14}H_2Br_8$, is formed in small quantity by prolonged heating of the preceding compound at 360° with bromine and iodine. It sublimes in dark-yellow needles, which are very sparingly soluble.

Trichloranthraquinone, $C_{14}H_5Cl_3O_2$, is obtained by heating anthraquinone at 180° in sealed tubes, with antimony pentachloride. It is a crystalline substance, melting at 284—290°, and dissolving in acetic acid, chloroform, and toluene.

Tetrachloranthraquinone, $C_{14}H_4Cl_4O_2$, is produced by heating dichloranthraquinone at 200—220°, with six times its weight of antimony pentachloride. It sublimes in yellow feathery crystals, which melt at 320—330°, dissolves in chloroform, toluene, carbon bisulphide, and boiling acetic acid, and are not affected by hot alcoholic potash or strong sulphuric acid. The same compound is formed on boiling hexchloranthracene with potassium dichromate and sulphuric acid:—

$$C_{14}H_4Cl_6 + O_2 = C_{14}H_4Cl_4O_2 + Cl_2.$$

Pentachloranthraquinone, $C_{14}H_3Cl_5O_2$, is produced in small quantity by heating anthraquinone at 250° with seven or eight parts of antimony pentachloride, or more easily by the oxidation of heptachloranthracene. It is an extremely stable body, insoluble in most liquids. It sublimes without melting.

Tribromanthraquinone, $C_{14}H_5Br_3O_2$, formed by heating anthraquinone at 275° with bromine and iodine, is an easily soluble substance, melting at 186°, and subliming at a higher temperature in small yellowish needles.

Tribromanthraquinone, when heated to 200° with sodium hydrate, is converted into purpurin, in accordance with the equation—

$$C_{14}H_5Br_3O_2 + 3NaOH = C_{14}H_5(OH)_3O_2 + 3NaBr.$$

The yield of purpurin is over 75 per cent. of the theoretical amount. With potash, instead of soda, the product is mainly oxypurpurin, $C_{14}H_4(OH)_4O_2$. This substance does not melt at 290°, but sublimes in brown flocks at a higher temperature. It is soluble in acetic acid, and nearly insoluble in alcohol and water. Its acetyl-compound melts above 240°.

Tetrabromanthraquinone, $C_{14}H_4Br_4O_2$, is obtained by heating the tribromo-compound at 320° with bromine, or better by oxidising hexabromanthracene with chromic acid. It crystallises from chloroform, carbon bisulphide, or nitrobenzene in yellow scales, which melt at 295—300°.

Tetrabromanthraquinone, when heated at 210° with sodium or potassium hydrate, yields a colourless trioxyanthraquinone, $C_{14}H_5(OH)_3O_2$, differing apparently from all known compounds of that formula.

Pentabromanthraquinone, $C_{14}H_3Br_5O_2$, is formed in very small quantity when anthraquinone is heated at 350° with iodine bromide. It is best obtained by the oxidation of heptabromanthracene. It crystallises in light needles, which dissolve easily in chloroform and carbon bisulphide, and sublime without melting.

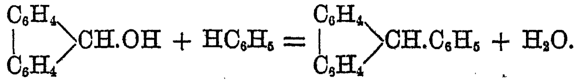
Pentabromanthraquinone, when fused with potassium hydrate, exchanges a part only of its bromine for hydroxyl, the products being apparently mixtures of tetrabromoxy-, tribromodioxy-, and dibromotrioxy-anthraquinone, varying with the temperature. J. R.

Diphenolethane. By R. FABINYI (*Deut. Chem. Ges. Ber.*, xi, 283—286).—All attempts hitherto made to prepare this body by the action of dehydrating agents in a mixture of phenol and aldehyde have failed. The author finds, however, that if tin tetrachloride be added in small quantities to a mixture of phenol and paraldehyde, until the product emits vapours of the tetrachloride, a brownish-red resinous mass is obtained. This mass, after being freed from phenol by boiling with water and distilling in a current of steam, is distilled under reduced pressure, when it yields a crystalline body containing some phenol, from which it is freed by boiling with ligroïn and crystallisation from benzene. It separates from the latter in colourless, concentrically-grouped needles, apparently containing benzene, and having the composition $2(C_{14}H_{14}O_2)C_6H_6$. When crystallised from water, it forms white, shining plates, having the composition

$CH_3.CH{=}(C_6H_4OH)_2$, which melt at 122° to a colourless liquid, but begin to decompose at 180°, and carbonise at 230°. It is easily soluble in soda and ammonia, and is reprecipitated from these solutions by acids. Its aqueous solutions give with basic lead acetate a voluminous white precipitate, which dissolves in acetic acid. Ferric chloride gives a yellowish-brown precipitate; nitrous acid a yellowish-green coloration: warmed with a dilute ammoniacal silver solution, it gives a mirror of the metal, whilst aldehyde is formed.

Dibenzoyldiphenolethane, $CH_3.CH = (C_6H_7O.COC_6H_5)_2$, is formed by boiling diphenolethane with benzoyl chloride; crystallised from alcohol, it forms slender, shining, yellowish-white needles, which melt at 152°, and resolidify at 90°. It is soluble in warm ether, and with difficulty in benzene. It is, however, most easily soluble in acetone, from which it crystallises in prisms. The composition of this compound shows that two hydroxyl groups exist in diphenolethane. P. P. B.

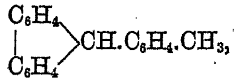
Synthesis of Diphenylene-phenylmethane and Diphenylene-tolylmethane. By W. Hemilian (*Deut. Chem. Ges. Ber.*, xi, 202—204).—Fluorenyl alcohol, when dissolved in benzene and heated to 140—150° with phosphorus pentoxide in sealed tubes, is converted into a dark-red resinous mass, which yields by distillation a hydrocarbon, crystallising from acetic acid in long silky needles, and melting at 145·5°. The formation and constitution of this substance (*diphenylene-phenylmethane*) is expressed by the equation—



$$\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>CH.OH + HC_6H_5 = \begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>CH.C_6H_5 + H_2O.$$

Diphenylene-phenylmethane is sparingly soluble in alcohol and ether, but dissolves freely in boiling acetic acid and in benzene. It does not combine with picric acid.

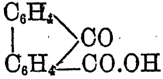
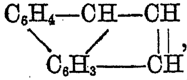
On substituting toluene for benzene in the above reaction, the product is a hydrocarbon melting at 128°, and agreeing in composition with the formula—



$$\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>CH.C_6H_4.CH_3,$$

which is that of *diphenylene-tolylmethane*. This substance crystallises in fine silky needles, and otherwise closely resembles the preceding compound. Its vapour-density was found to be 8·75 (theory requiring 8·86).

Some other hydrocarbons, formed together with the foregoing, are being examined by the author. J. R.

Fluoranthrene, a New Coal-Tar Hydrocarbon. By R. Fittig and F. Gebhard (*Deut. Chem. Ges. Ber.*, x, 2141).—In working up a quantity of higher coal-tar distillate for phenanthrene, a crystalline mass was obtained which did not yield phenanthrene-derivatives on oxidation, but contained much pyrene, and in addition a little of a new hydrocarbon, forming a picric acid compound difficultly soluble in alcohol, and separable from pyrene only by laborious crystallisations, &c. When pure, this body fuses at 109°, and gives numbers agreeing with the formula, $C_{15}H_{10}$; the picric acid derivative, $C_{15}H_{10}.C_6H_3(NO_2)_3O$, melts at 182—183°. Fuming nitric acid forms a trinitro-derivative, whilst chromic acid gives rise to a quinone not yet fully investigated, and a well-defined acid, $C_{14}H_8O_3$, the barium salt of which is $(C_{14}H_7O_3)_2Ba + 4H_2O$, and the calcium salt $(C_{14}H_7O_3)_2Ca + 2H_2O$. This acid melts at 191—192°, and on distillation with zinc-dust is converted almost quantitatively into *fluorene.* Heated with soda-lime, it yields *diphenyleneketone,* $C_{14}H_8O_3 = CO_2 + C_{13}H_8O$, whence the acid has the structure , and the hydrocarbon is probably indicated by , standing to fluorene in the same relationship as phenanthrene to diphenyl, whence the name *fluoranthrene.*

Apparently the body has been already obtained by Goldschmidt, who has recently described such a substance in his memoir on idryl.

Pure pyrene melts at 148—149°, the mononitro-derivative at 149·5—150·5°, and the picric acid compound at 222°. So long as it contains no other hydrocarbons, it forms compact, shining monoclinic prisms; but if impure, it forms little plates. Graebe did not obtain it in a state of perfect purity. Diphenylenemethane from diphenylene ketone is identical with fluorene. C. R. A. W.

Action of Sodium on Chinoline and Lepidine. By C. G. WILLIAMS (*Chem. News*, xxxvii, 85).—When sodium amalgam is added to chinoline or lepidine, the mixture becomes hot, turns reddish-brown, and then solidifies. On adding water, a yellowish oil separates, which gives a deep reddish-brown solution when boiled with water and an acid, and deposits scarlet crystals on cooling. The scarlet colour is altered by exposure to light, and the same action occurs on silk or wool which has been dyed with the substance. It appears to be hydrochloride of di-chinoline, $C_{18}H_{14}N_2,HCl$. When lepidine was similarly treated and the resulting oil boiled with dilute nitric acid, red crystals were formed, which proved to be nitrate of lepidine, $C_{20}H_{18}N_2,HNO_3$. A. J. C.

Nicotine. By R. LAIBLIN (*Deut. Chem. Ges. Ber.*, x, 2136).—Pure nicotine boils at 240—242° (uncorrected). When oxidised by permanganate of potassium, added until no more is decolorised (10 grams nicotine in 500 c.c. of water require about 60 grams of permanganate dissolved in 2,000 c.c. of water), it yields carbonate and *pyridene-carbonate* of potassium. Free pyridene-carbonic acid, $C_6H_5NO_2$, or $C_5H_4N.COOH$, is obtained by filtering the solution from manganese dioxide, evaporating to dryness, taking up with alcohol, converting the dissolved potassium salt into silver salt, and decomposing it with sulphuretted hydrogen. After crystallisation from hot alcohol or water, it forms colourless crystals, melting at 225—227° (uncorrected), and only sparingly soluble in ether and chloroform. The author has analysed the free acid, its platino-chloride,

$(C_6H_5NO_2.HCl)_2PtCl_4 + 2H_2O$, the potassium and silver salts, the hydrochloride, $C_6H_5NO_2.HCl$, and the calcium salt, $(C_6H_4NO_2)_2Ca + 5H_2O$, and finds numbers uniformly agreeing with the formula, $C_6H_5NO_2$, originally proposed by Huber (who prepared his pyridene-carbonic acid by oxidising nicotine with chromic acid liquor), and not agreeing at all with the formula, $C_{10}H_8N_2O_3$, proposed by Weidel, who employed nitric acid as oxidiser. On repeating Weidel's experiments, the acid obtained melted at the same temperature as that prepared by means of permanganate.

On distillation with lime, 20 grams of undried potassium salt gave nearly 5 grams of pure pyridine. C. R. A. W.

Constituents of Pereiro-Bark. By O. Hesse (*Deut. Chem. Ges. Ber.*, x, 2162).—The bark of pereiro, also called *Pinguaciba* and *Canudo Amargoso*, is employed in Brazil as a febrifuge. According to Correados and Santos, also Goos, an amorphous alkaloïd is contained therein, which they termed *Pereirine.* Peretti has obtained this base in a crystallised condition, whilst Rochefontaine and De Freitas have examined its physiological action, and found it highly poisonous. They propose to term this alkaloïd *Geissospermine*, as the tree furnishing the bark is one of the Apocyneæ, either *Geissopermum Vellosii* or *G. leve.* The author finds that two alkaloïds are really present: one crystallisable in small prisms, readily soluble in alcohol, almost insoluble in water and ether, precipitable by potash or ammonia from its solution in acids in amorphous flakes, soon becoming crystalline. To this he applies the term "geissospermine." The other is readily soluble in ether and is amorphous; this he names "pereirine."

Geissospermine, when crystallised, is indicated by $C_{19}H_{24}N_2O_2,H_2O$. It forms an insoluble amorphous platinochloride; the aurochloride is a brown-yellow precipitate, not containing any reduced gold. Concentrated nitric acid dissolves it with a purple-red colour. Concentrated sulphuric acid, when pure, dissolves it, forming a colourless fluid, which rapidly becomes blue. Ordinary acid, or acid containing iron, dissolves it to a blue liquid. Concentrated hydrochloric acid gives no coloration. The alkaloïd loses its water of crystallisation, giving a yellowish mass, which browns on further heating, fusing at 160°, and solidifying on cooling.

Pereirine does not appear to have been analysed as yet. Strong nitric acid colours it blood-red; pure sulphuric acid violet-red.

C. R. A. W.

On the Alkaloïd termed Quinidine by Henry and Delondre. By O. Hesse (*Deut. Chem. Ges. Ber.*, x, 2149).—The substances described as "quinidine" by Henry and Delondre, in 1833 and 1834, and by Winckler, in 1844, are regarded by the author as more or less pure cinchonidine (isomeric with cinchonine, $C_{20}H_{24}N_2O$); the "quinidine" of Van Heijningen, isomeric with quinine, $C_{20}H_{24}N_2O_2$ (known in England as *quinidine*), he prefers to term "conchinine," although what advantage is to be derived from the use of this term does not appear, inasmuch as by its employment the relationship of the alkaloïd to quinine, parallel with that of cinchonidine to cinchonine, is not indicated. C. R. A. W.

Hydro-derivatives of Cinchonine. By Z. H. SKRAUP (*Deut. Chem. Ges. Ber.*, xi, 311—315).—The chief products of the oxidation of cinchonine by potassium permanganate are cinchotenine and formic acid.

$$\underset{\text{Cinchonine.}}{C_{19}H_{22}N_2O} + O_4 = \underset{\text{Cinchotenine.}}{C_{18}H_{20}N_2O_3} + CH_2O_2.$$

The hydrocinchonine, $C_{19}H_{24}N_2O$ (m. p. 267°), obtained as a bye-product in this reaction (Caventou and Willm, *Ann. Chem. Pharm. Suppl.*, vii, 378), cannot be regarded as a true hydroderivative of cinchonine, since the action of nascent hydrogen on cinchonine gives rise to quite different products.

Zorn (*J. pr. Chem.* [2], viii, 279) obtained two hydrocinchonines by the action of sodium amalgam on cinchonine, viz., a crystalline body, to which he gave the formula, $C_{20}H_{26}N_2O$, and an amorphous substance, $C_{20}H_{28}N_2O$. Similar results are obtained with zinc and sulphuric acid, but the reaction is not so complete.

The action of nascent hydrogen does not convert the crystalline into the amorphous hydrocinchonine. The crystalline body is *dihydrodicinchonine*, $(C_{19}H_{22}N_2O)_2.H_2$.

The amorphous hydrocinchonine was not obtained in a state of purity; it is deposited in the form of yellow tabular crystals, when caustic potash is added to a dilute solution of the body in hydrochloric acid.

In conclusion the author expresses his belief that O. Hesse's homocinchonidine (*Deut. Chem. Ges. Ber.*, x, 2156) is identical with cinchonidine.

W. C. W.

Alkaloïds of Cinchona Bark. By O. HESSE (*Deut. Chem. Ges. Ber.*, x, 2152).—The author regards the body described by Koch as "cinchonidine," as being a lower homologue of true cinchonidine (the so-called quinidine of Winckler), and hence proposes to term it *homocinchonidine*. The salient characters of the cinchona alkaloïds may be thus contrasted:—

A. QUININE GROUP.—*Quinine*, $C_{20}H_{24}N_2O_2$, precipitated as an amorphous hydrate containing $3H_2O$, by alkalis. The crystallised anhydrous base melts at 177°, the trihydrate at 57°; the former is soluble in 1960, the latter in 1670 parts of water, at 15°. Solutions in sulphuric acid fluoresce; those in hydrochloric acid do not (addition of metallic chlorides, &c., often prevents fluorescence). Chlorine and ammonia give the thalliochin reaction. The hydrochloride is $C_{20}H_{24}N_2O_2.HCl.2H_2O$; the neutral sulphate $(C_{20}H_{24}N_2O_2)_2.H_2SO_4.8H_2O$, and the acid sulphate, $C_{20}H_{24}N_2O_2.H_2SO_4.7H_2O$. Pure quinine sulphate gives no precipitate by the following mode of testing, which is useful as a means of indicating the presence of other alkaloïds (Kerner); 1 part of sulphate is shaken to an emulsion with 10 of water at 12—15° C., and the whole left to itself for half an hour; to 5 c.c. of filtrate, 7 of ammonia solution, sp. gr. 0·96, are added, and the whole mixed; this test will detect 1 per cent. of cinchonidine. Quinine is lævo-rotatory.

Quinidine (called by the author "conchinine"), $C_{20}H_{24}N_2O_2$, crystallises from alcohol in prisms, with $2\frac{1}{2}H_2O$; from ether in rhombohedrons, with $2H_2O$; and from boiling water in thin plates, containing $1\frac{1}{2}H_2O$; neither of the last two kinds of crystals effloresce in the air. Dextro-rotatory. The hydrochloride is $C_{20}H_{24}N_2O_2.HCl.H_2O$; the neutrasulphate $(C_{20}H_{24}N_2O_2)_2.H_2SO_4.2H_2O$; and the acid sulphate, $C_{20}H_{24}N_2O_2.H_2SO_4.4H_2O$.

Quinicine, isomeric with quinine and quinidine, $C_{20}H_{24}N_2O_2$, produced from either of these alkaloïds by heating certain of their salts; the monosulphate forms it without loss of weight on fusion. Feebly dextro-rotatory. Amorphous, but can give rise to certain crystalline salts; not contained in cinchona barks.

Apo-diquinicine (diconchinine of the author); is related to quinine and its isomerides, as indicated by the equation—

$$2C_{20}H_{24}N_2O_2 = H_2O + C_{40}H_{46}N_4O_3.$$

This base constitutes the greater portion of the amorphous bases constituting the "quinoidine" of commerce; it is wholly amorphous, and forms only amorphous salts. The sulphuric acid solution fluoresces; it gives the thalliochin reaction, and is feebly dextro-rotatory [whence evidently it is an anhydro-derivative of quinicine, and is not improbably formed by alteration and dehydration during extraction, like certain analogous derivatives of the active alkaloïds of the aconites.—C. R. A. W.].

B. CINCHONINE GROUP.—*Cinchonine*, $C_{20}H_{24}N_2O$, crystallises anhydrous from alcohol; no fluorescence in sulphuric acid solutions; the hydrochloride is $C_{20}H_{24}N_2O.HCl.2H_2O$, and the sulphate, $C_{20}H_{24}N_2O.H_2SO_4.2H_2O$; the former crystallises in long needles; the latter in compact prisms. Dextro-rotatory.

Cinchonidine (the "quinidine" of Henry and Delondre, and of Winckler; the α-quinidine of Kerner), $C_{20}H_{24}N_2O$, isomeric with cinchonine. Crystallises from alcohol in anhydrous needles, and prisms or plates. No fluorescence (when pure). No thalliochin reaction. Lævo-rotatory. The hydrochloride is $C_{20}H_{24}N_2O.HCl.H_2O$, and the sulphate $(C_{20}H_{24}N_2O)_2.H_2SO_4.6H_2O$.

Cinchonicine, $C_{20}H_{24}N_2O$, is produced from either of its isomerides, cinchonine or cinchonidine, in the same way as quinicine from quinine or quinidine. Amorphous, but forms some well crystallised salts. Not contained in cinchona barks. Dextro-rotatory.

Dicinchonicine (termed diconchonine by the author). An amorphous base contained in commercial "quinoidine," derived from barks which contain much cinchonine or cinchonidine. Has not yet been obtained quite pure, but is probably $C_{40}H_{48}N_4O_2$.

[Query, an alteration-product formed during manufacture, like apo-diquinicine?—C. R. A. W.]

C. HOMOCINCHONINE GROUP.—*Homocinchonine*, $C_{19}H_{22}N_2O$. The author views the "cinchonine" obtained by Skraup (*Chem. Centr.*, 629 [1877]) from *C. rosalenta*, as having this composition.

Homocinchonidine, $C_{19}H_{22}N_2O$ (the "cinchonidine" of Koch, *Pharma-*

ceutische Post, x, 207 [1877]), crystallises from alcohol in large prisms and small plates. Lævo-rotatory. A solution of 2 grams in 100 c.c. of 97 per cent. alcohol at 15°, gives the value—

$$(\alpha)_D = -109\cdot34.$$

The hydrochloride is $C_{19}H_{22}N_2O.HCl.H_2O$, and the sulphate,

$$(C_{19}H_{22}N_2O)_2.H_2SO_4.6H_2O.$$

This alkaloïd has been mistaken for aricine, owing to the circumstance that its sulphate, under certain conditions, separates as an amorphous mass, instead of slender needles.

Homocinchonicine, $C_{19}H_{22}N_2O$, is derived from homocinchonidine, just as cinchonicine and quinicine are derived from their respective isomerides, by heating the sulphates, &c. Amorphous, but forms a crystalline oxalate, $(C_{19}H_{22}N_2O)_2.C_2H_2O_4.4H_2O$, remarkably like that of cinchonicine.

Dihomocinchonicine (dihomocinchonine of the author), $C_{38}H_{43}N_4O_2$, accompanies the homocinchonine alkaloïds in *C. rosalenta.* Strongly dextro-rotatory. Amorphous; furnishes only amorphous salts.

D. QUINAMINE GROUP.—*Quinamine*, $C_{19}H_{24}N_2O_2$. Occurs in the bark of *C. succirubra*, from Darjeeling, and other localities in British India and Java; in the "*Cinchona rouge de mutis*," of Delondre; in *C. nitida*, *C. erythranthra*, *C. erythroderma*, *C. rosalenta*, *C. calisaya.* var. *Schuhkrafft;* and *C. calisaya.* Difficult to separate from the amorphous alkaloïds; the separation may, however, be effected by means of potassium thiocyanate added to the solution of the mixed bases in acetic acid until the liquid is almost decolorised, when most of the amorphous bases are precipitated, with but little quinamine; on treating the residue left by the evaporation of the ethereal extract with ammonia and ether, and dissolving in alcohol, a liquid is obtained, from which quinamine crystallises on standing. The author formerly assigned to it the formula, $C_{20}H_{26}N_2O_2$, but now modifies that formula by subtracting CH_2. M. p. 172°.

Quinidamine (termed conquinamine by the author), accompanies quinamine in *C. succirubra* and *rosalenta* barks; crystallises in long shining prisms, melting at 123°. Dextro-rotatory. A solution of 1·8 grams in 100 c.c. of 97 per cent. alcohol, gives the value at 15° $[\alpha]_D = +200$. Only precipitated by platinic chloride in concentrated solutions; the gold salt soon decomposes; the hydriodide crystallises in fine prisms.

Quinamidine and *quinamicine*, two amorphous bases, formed by heating quinamine with dilute sulphuric acid. Isomeric with quinamine. The hydrochlorides are crystalline, and the difference between the two is not clearly stated. By continuing the action of sulphuric acid at 120—130°, a brownish, non-crystalline base is formed, precipitable by sodium carbonate, and insoluble in ether. The author states that this is indicated by the formula, $C_{17}H_{20}N_2O_2$, and terms it *Proto-quinamicine.*

Apoquinamine, $C_{19}H_{22}N_2O$, isomeric with homocinchonidine. Prepared from quinamine or quinidamine by boiling for a short time with hydrochloric acid; hydrobromic acid first produces the same anhydro-derivative, and subsequently converts it into a resinous, difficultly soluble hydrobromide; no methyl bromide is evolved during the reaction. The first reaction by which apoquinamine is formed is, $C_{19}H_{24}N_2O_2 = H_2O + C_{19}H_{22}N_2O$. Apoquinamine is a white, amorphous powder, readily soluble in ether, alcohol, and dilute hydrochloric acid, the last solution precipitating with strong hydrochloric, or better, nitric acid. The hydrochloride, platinum salt, and gold salt, are amorphous.

E. OTHER ALKALOÏDS.—*Paricine*, $C_{16}H_{18}N_2O$, an amorphous base, forming amorphous salts, occurring with quinamine in *C. succirubra* bark, from Darjeeling. On keeping, it becomes less readily soluble in ether.

Paytine, $C_{21}H_{20}N_2O.H_2O$, in Payta bark, crystallises in fine prisms. Heated with soda lime, it furnishes a substance, *paytone*, crystallisable in yellow plates. Lævo-rotatory.

Paytamine, an amorphous alkaloïd, accompanying paytine.

Cusconine, $C_{23}H_{26}N_2O_4.2H_2O$, crystallises in plates; the neutral sulphate is amorphous, and does not dissolve readily on addition of more acid.

Aricine, $C_{23}H_{26}N_2O_4$, isomeric with cusconine, and accompanying that base. Crystallises in white shining prisms, melting at 188°. Lævo-rotatory. The salts are sparingly soluble.

Cusconidine, an amorphous alkaloïd, accompanying cusconine.

Javanine, not yet fully examined, forms a crystallisable oxalate. Occurs in *C. calisaya var. javanica*.

Bolivia calisaya bark contains a fluid alkaloïd, possessing a peculiar odour, like that of quinoline. C. R. A. W.

Coloured Crystalline Compounds from Brucine. By D. LINDO (*Chem. News*, xxxvii, 98).—Sulphurous acid and other reducing agents convert the yellow nitro-compound which is formed by the action of nitric acid on brucine, into a violet crystalline substance, which may be readily obtained by heating brucine with concentrated nitric acid until it becomes yellow, and then adding sulphurous acid solution in excess. A yellow crystalline nitrate of another base is also obtained in minute crystals on heating brucine with nitric acid, as above, allowing it to cool, and adding alcohol. These two coloured compounds are readily converted into each other by the addition or removal of oxygen. The violet crystals dissolve in a strong solution of potassium hydrate, with an intense blue colour, which quickly changes to yellow, the mixing of the two colours producing a fine green. The reaction is very delicate. A. J. C.

Volatile Constituents of Human Excrement. By L. BRIEGER (*Deut. Chem. Ges. Ber.*, x, 1027—1031).—The author examined the fæces of healthy persons and of convalescents, and found, in addition to acetic, butyric, and isobutyric acids, small quantities of phenol and indol, and a new crystallisable body, which he terms *skatol* (τὸ σκατὸς :

fæces). It crystallises in irregularly-dentate, shining plates, resembling indol, which, by frequent recrystallisation from hot water, can be obtained snow-white. The crystals, which have a highly disagreeable, fæcal odour, melt at 93° to 95° C. Skatol is rather less soluble in water than indol, and can be easily distinguished from the latter by not being coloured by chlorine water, and by the fact that an aqueous solution of skatol, treated with a drop of fuming nitric acid, does not give a red precipitate, but a white cloudiness. It is soluble in warm dilute nitric acid, but separates unchanged on cooling. It is decomposed when boiled with nitric acid for some time, and vapours smelling of nitrophenol are given off. As the elementary analysis of different specimens did not give concordant results, the author cannot assign any formula to it at present. Skatol forms the chief constituent of the volatile aromatic components of human fæces. Fæces of dogs (whether fed on meat or bread diet) contained no skatol, but indol, and in addition a yellow oil, with a revolting and peculiarly irritating smell. The author has not yet been able to analyse this yellow oil, although it forms the chief volatile constituent of dogs' fæces. He has repeatedly obtained it by distillation from human pathological fluids. In the pancreas after putrefaction, and in the fæces of typhus patients, no skatol was found. The author considers skatol identical with the substance which Secretan obtained by the decomposition of egg-albumin under water for six months.

Skatol injected under the skin of rabbits, passes out in the urine as a substance yielding colouring matter. Skatol is, according to the author, the unknown substance in human urine to which Jaffé attributes the red or violet colour on the addition of hydrochloric acid and chloride of lime. The addition of hydrochloric acid to the urine of rabbits, after a hypodermic injection of skatol, immediately produces a violet coloration, whereas previously the animal's urine showed no change on the addition of either hydrochloric acid or chloride of lime. Phenol, the author finds, is a constant component of human fæces. The above results show that the specific products of decomposition are normal components of intestinal digestion. E. C. B.

Preparation of Œnolin. By E. Varenne (*Bull. Soc. Chim.* [2], xxix, 109—110).—Œnolin, the red colouring matter of wine, may be obtained by mixing the wine with lime to the consistency of a paste, which is drained on a funnel. The residue containing the colouring matter is mixed with alcohol of 95 per cent., and treated with sufficient sulphuric acid to neutralise the lime and decompose the compound of lime with the colouring matter. The solution is filtered from calcium sulphate, and on evaporation leaves œnolin as a black powder, which, when bruised, exhibits a crimson-red colour resembling powdered cochineal. Sub-acetate of lead may be used instead of lime.

L. T. O'S.

Distillation of some Resins and Resin-acids with Zinc-dust. By G. Ciamician (*Deut. Chem. Ges. Ber.*, xi, 269—276).—By the distillation of a mixture of crystallised abietic acid with ten times its weight of zinc-dust in a stream of hydrogen, a heavy brown oily product was obtained, which, on re-distillation in a current of steam, yielded a yellow oil lighter than water, whilst a dark-brown viscous tar-like mass remained behind. The light oil, when submitted to repeated fractional distillation and treatment with sodium, was separated into toluene boiling at 110—112°, meta-ethylmethylbenzene, C_9H_{12}, boiling at 158°, and naphthalene, together with a small quantity of methylnaphthalene. The portion remaining behind, on distilling in a current of steam, was again distilled with zinc-dust, and a yellow oil obtained, which, on cooling, deposited a mass of crystals. This yellow oil was found to contain naphthalene and methylnaphthalene, $C_{11}H_{10}$, the latter boiling at 230—232°, and yielding on oxidation an isonaphthoic acid melting at 182°. The hydrocarbon forms with picric acid a compound, $C_{11}H_{10}+(C_6H_3(NO_2)O$, which crystallises in fine yellow needles melting at 116—117°. The boiling point agrees with that of the methylnaphthalene prepared by Fittig and Remsen (*Ann. Chem. Pharm.*, clv, 112). The crystalline body on purification yielded a substance crystallising in yellow plates, subliming easily, and melting at 190°. Analyses and vapour-density show that its composition is $C_{15}H_{12}$, and when oxidised with chromic acid it yields an anthraquinone-carbonic acid, $C_{15}H_8O_4$, crystallising in pale-yellow needles and melting at 278—280°, thus showing the hydrocarbon to be a methylanthracene, and probably identical with that prepared by Fischer and Weiler. The amount of methylanthracene formed is very small and due to a secondary action.

Colophony when similarly treated yields the same products; toluene is, however, formed in much smaller quantities.

Gum benzoin distilled with zinc-dust yields toluene, naphthalene, and methylnaphthalene, together with a small quantity of xylene, which is probably orthoxylene.

The author intends to submit other resins to a similar investigation.

P. P. B.

An Indifferent Crystalline Resin from Gurjun Balsam. By F. A. Flückiger (*Arch. Pharm.* [3], xii, 58—61).—From the residue remaining in the preparation of a large quantity of gurjun balsam the author has obtained a crystalline substance, which at first was thought to be copaivic acid, but on examination it was found to possess neutral properties. It was obtained by crystallisation from petroleum spirit in prismatic crystals, which melt at 126—130°. It forms no compounds with bases, or crystalline derivatives with acetic or nitric acid. By dry distillation this substance gave an oil which was unaffected by ferric chloride. It is dissolved by sulphuric acid with a reddish-yellow colour, and is reprecipitated by water; it is unaltered by fusion with potassium hydrate.

The angular measurements of the crystals, which belong to the asymmetric system, are given in detail.

The formula of this body is $C_{28}H_{46}O_2$.

A. J. C.

Elemic Acid. Contribution to the Chemistry of Elemi. By E. Buri (*Pharm. J. Trans.* [3], viii, 601).—In addition to the two crystalline substances, bryoïdin (Fluckiger, *Pharm. J. Trans.*, Aug. 22, 1874) and amyrin (Buri, *idem.*, Aug. 19, 1876), that have been isolated from elemi, the author has obtained a crystalline body, elemic acid, from the brown amorphous resin remaining in the alcoholic mother-liquors from which amyrin has been crystallised. The resin is dissolved in ether and shaken with potassium hydrate, then with water to dissolve the potassium elemate, from which elemic acid can be precipitated by hydrochloric acid.

Elemic acid has been obtained in crystals, much larger than those of bryoïdin and amyrin, by crystallisation from alcohol. It melts at 215° to an amorphous mass. It is soluble in ether and in 17·55 parts of alcohol, sparingly so in carbon bisulphide, but insoluble in water. The solution of elemic acid is lævogyrate, deviating the ray 3·5°. Its alcoholic solution reddens litmus. Its formula is $C_{35}H_{56}O_4$ or $(C_5H_8)_7O_4$, thus showing elemic acid to be allied to bryoïdin, amyrin, and other derivatives of terpene, C_5H_8. With the exception of the potassium salt, which crystallises in needles and has the composition expressed by the formula $C_{35}H_{55}O_4K.18H_2O$, the metallic elemates are amorphous, and are obtained by double decomposition from the potassium salt.

An amorphous resin of acid character, and a so-called indifferent amorphous resin are also among the constituents of elemi, forming indeed the chief part of the elemi of Manila. A. J. C.

Maté or Paraguay Tea. By H. BYASSON (*Pharm. J. Trans.* [3], viii, 605).—Maté tea is yielded by the *Ilex Paraguayensis* or *Ilex maté* of South America, where maté constitutes the favourite drink. The variety examined was the greenish-yellow powder, which is prepared by the natives from the roasted and coarsely-powdered leaves. The analysis was made by mixing the maté with lime and successively exhausting the mixture with chloroform and alcohol. 100 grams gave:—

Caffeine	1·85
Glutinous substance, &c.	3·87
Complex glucoside	2·38
Resin	0·63
Inorganic salts, including iron	3·92
Malic acid	not estimated.

Exhausted with boiling water the tea gave 24 per cent. dry extract, and 3·92 per cent. of ash in the extract, calculated on the maté taken. The ash contained potassium carbonate and much sulphuric acid. The test for tannin and caffetannic acid gave negative results.

The amount of caffeine is comparable with that in the kinds of tea and coffee richest in that alkaloïd. A. J. C.

Physiological Chemistry.

Experiments on the Digestibility and Nutritive Power of Meat-flour. By WOLFF, FUNKE, and DITTMANN (*Landw. Versuchs. Stat.*, xx, 180—182).—When, besides steamed potatoes, various quantities of American meat-flour were given to pigs, it was found that on an average 96·6 per cent. of the albumin and 87·3 per cent. of the fat contained in the latter were digested, and these coefficients were independent of the ratios in which the two kinds of food were administered. When on the other hand, besides a constant weight of potatoes, meat-flour and wheat-flour were given in the ratio 1 : 1·5—2·8, only 86·6 per cent. of the meat-flour albumin was digested, and the percentage rose again when starch was omitted from the diet.

Young pigs fed on potatoes increased in weight 1 kilo. for each 13 kilos. of potatoes ingested; the same increase in weight was produced by 1·8 kilos. of meat-flour; hence the nutritive value of the latter is to that of the former as 7·2 : 1. In older animals (70 kilos. in weight) 34·6 kilos. of potatoes or 1·21 kilos. of meat-flour produced an increase of weight equal to 1 kilo.; that is, 28·6 kilos. of potatoes had the same effect as 1 kilo. of meat-flour, or the nutritive value of the latter was relatively four times as great as in the former experiments. In determining the value of food-stuffs, therefore, it is clear that no reliance can be placed on isolated experiments, since many circumstances may affect the results.

In two other sets of experiments the same increase in weight, 100 kilos., was produced, on the one hand by 1,451 kilos. of potatoes with 44 kilos. of meat-flour, and on the other hand by 1,163 kilos. of potatoes with 104·5 kilos. of meat-flour, the total amount of dry matter in the two diets being the same. Above a certain limit, then, dry potato-substance is as nourishing as dried meat-flour, the latter being only advantageous when added to the former (or other foods poor in nitrogen) in sufficient quantity to afford a moderately nourishing diet (albumin to other organic matters as 1 : 5).

The authors have also found that vegetable and animal albumin are nutritive in nearly the same degree. This was proved by feeding animals—1st, on a diet composed of potatoes and peas, with a little linseed; and 2nd, on a diet of potatoes, meat-flour, and starch, the total weight of digestible substances being the same in both, and the ratio of albumin to other organic matters 1 : 6. When starch was omitted from the second diet, and the amount of meat-flour increased so as to make the ratio of albumin to fat and carbohydrates greater than 1 : 4·5 (the total organic matter being still the same), no additional advantage resulted. Ch. B.

Formation and Secretion of Ferments. By P. GRÜTZNER (*Pflüger's Archiv. f. Physiologie*, xvi, 105—123).—According to Nussbaum, solutions of ferments uniformly possess the power of reducing perosmic acid, and those glands which secrete fluids capable of setting up fermentative actions contain cells which are more or less darkened by that reagent, whilst glands, the secretions from which are non-fermentative, are unaffected by it. The author disputes the generality of this rule: thus, the submaxillary glands of rabbits produce more darkening with perosmic acid than the parotid glands, whilst the secretion of the former is non-fermentative and that of the latter highly fermentative, and similarly in other cases. C. R. A. W.

On the Excretion of Indican under Physiological and Pathological Conditions. By M. JAFFÉ (*Virchow's Arch.*, lxx, 72, and *Chem. Centr.*, 1877, 679).—The author found that in the urine of dogs, the indigo, of which there were mere traces on a diet poor in nitrogen, increased to such an extent when they were fed on horseflesh, that on an average 8 to 16 mgr. could be obtained daily. In a man dying of starvation from œsophageal cancer, the author found on the day of death 17 mgr. of indigo in the urine. The great increase of indigo in the urine accompanying obstruction of the small intestine the author explains as follows:—Indol only occurs in the later stages of pancreatic digestion, and as a product of decomposition; the previous products of digestion are in the normal state rapidly absorbed, so that but little indol can be formed. Stagnation of the contents of the small intestine, however, gives more opportunity for decomposition and for the formation of indol. As digestion occurs almost wholly in the small intestine in man and the carnivora, the author thinks that obstruction in the large intestine would not cause any other result than the stoppage by masses of fæcal matter. The effects would be felt in the small intestine after some time only. The author suggests that the excretion of indican may perhaps assist in the diagnosis of the situation of an intestinal obstruction. E. C. B.

On Lactosuria. By F. HOFMEISTER (*Chem. Centr.*, 1877, 663—667).—The author of this paper has isolated lactose in considerable quantities from the urine of lying-in women, and applies to this condition the term "lactosuria."

The urine was derived from a healthy woman in whom there was well-marked stoppage in the lactic secretion. The method adopted was in the main that of Leconte and Brücke, in which the sugar was precipitated by acetate of lead and ammonia. The substance thus obtained agreed with milk-sugar in regard to its crystalline form, melting point, amount of water of crystallisation, composition, optical activity, &c. The author thinks that during the stoppage of the secretion of milk, some constituents of that fluid, amongst them lactose, enter the blood, and then pass off by the kidneys. Large quantities of milk-sugar administered by the mouth to an adult gave rise to the presence of sugar in the urine in small quantities, but still distinctly appreciable by the polarimeter. E. C. B.

Formation of Hippuric Acid in the Kidneys. By A. HOFFMANN (*Chem. Centr.*, 1877, 409—416).—The author finds, from experiments on himself, that after the introduction of benzoic acid into the human organism, neither benzoic nor hippuric acid occurs in the perspiration. In one experiment in which benzoic acid alone was taken, benzoic acid was present in the urine in addition to the hippuric acid, whereas in another experiment in which benzoic acid and glycocine were taken, no benzoic acid, but only hippuric acid was detected in the urine, indicating apparently that a combination of the benzoic acid with the glycocine had taken place. The author further experimented by passing through fresh kidney removed from the body defibrinated blood containing, in addition to benzoic acid, alanine,

($C_3H_7NO_2$), when he obtained an acid crystallising in large white needles differing entirely in appearance from hippuric acid. He was unable with certainty to identify this substance with the hitherto unknown alanine-hippuric acid. Two experiments in which both leucine and benzoic acid were passed through the kidneys, showed that either these do not combine in the kidneys, or else that the compound, formed during the necessary manipulations for separating it from the solution, undergoes decomposition. Further experiments showed that no hippuric acid is formed on passing through the kidney blood containing benzoic acid and glycocine, and whose oxygen had been displaced by carbonic oxide; also, that the kidney, after removal from the body, and after blood saturated with carbonic oxide had been passed through it for two hours, still possessed the power of forming hippuric acid from benzoic acid and glycocine when they were dissolved in oxygenated blood. In order to show that the formation of hippuric acid from glycocinė and benzoic acid is a function of the living kidney, the author poisoned a fresh kidney, after its removal from the body, by passing through it blood containing quinine, and on the subsequent addition of benzoic acid and glycocine it was found that the amount of hippuric acid formed was very small, so that it is probable that if the kidney-tissue were completely modified by quinine poisoning, the power possessed by the kidney of forming hippuric acid would be quite extinguished. E. C. B.

Origin of Uric Acid in the Organism of Birds. By H. MEYER and M. JAFFÉ (*Deut. Chem. Ges. Ber.*, x, 1930—1933).—The authors gave urea to fowls with their food, in order to estimate the influence of this substance on the excretion of uric acid. From the first experiment, in which a fowl was fed with meat, it appears that of two grams of urea introduced, scarcely any appeared in the excretions, showing that in the organism of fowls urea undergoes transformation (a fact that was also discovered at the same time, independently, by Cech in Salkowski's laboratory). On the three days following the first administration of urea, a considerable increase in the uric acid took place, and the actual quantity of uric acid formed was very nearly that which it is calculated could be produced from the amount of urea ingested. This leads to the supposition that the urea was directly transformed into uric acid. Another explanation, however, may be given, viz., that the urea in the organism of birds is decomposed into carbonate of ammonia and ammonia salts, which, as v. Knieriem has shown, producing a considerable increase in the excretion of uric acid. In order to ascertain this the authors in another similar experiment estimated the amount of ammonia excreted. They found that after feeding with urea, the amount of ammonia is considerably increased, and they calculate that whilst one gram of urea was ingested, an amount of uric acid and ammonia, together corresponding to 1·16 grams of urea, were excreted. These results are also in favour of the supposition that the urea, as far as it is not excreted as ammonia salts, is directly converted into uric acid in the organism of birds. The authors draw this conclusion with all reserve, and do not consider the question as by any means finally settled. E. C. B.

Conversion of Uric Acid into Urea in the Body of the Dog. By C. Voit (*Zeitschr. für Biologie*, xiii, 530—532).—The following experiments were conducted by the author in conjunction with Zabelin:—14 and 30 grams of uric acid were administered on two consecutive days to a large dog which had for some time previously been fed on meat. Urea in abnormal quantity was detected in the urine for five days, the total excess amounting to 28 grams, which the author concludes to have been derived from the uric acid. Of the latter only 3·72 grams passed into the fæces. On two days the excess of urea in the urine amounted to 8·95 grams = 4·18 grams of nitrogen. Since other substances than urea are precipitated by mercuric nitrate (by means of which the estimations were made), the ratio of nitrogen calculated from urea, to the total nitrogen yielded on ignition with soda-lime, was also determined, both before and during the action of the uric acid. As the ratio was nearly the same in both periods, the author concludes that by far the greater part of the uric acid was converted into urea. A special examination was made by Zabelin for allantoïn, but without success.

These results do not agree with those of Salkowski (*Deut. Chem. Ges. Ber.*, ix, 719; *Zeitschr. für physiologische Chemie*, i, 4).

Ch. B.

Chemistry of Vegetable Physiology and Agriculture.

New Researches on the Functions of Fungi and their Property of Inverting Cane-sugar. By A. Béchamp (*Compt. rend.*, lxxxvi, 355—358).—The author is of opinion that the view is restricted which regards sugar as the necessary source of alcohol in fermentation, and microscopic plants as the only producers of alcoholic fermentation. He has shown that an aqueous solution of sodium acetate, or of ammonium oxalate, furnishes alcohol with certain moulds. Yeast from beer, perhaps all yeasts, produce alcohol in distilled water, without the presence of sugar. The following new facts support this physiological theory of fermentation:—

I. Normal urine, destitute of glucose, when undergoing ammoniacal fermentation, forms at the same time alcohol and acetic acid. In one of these fermentations the ferment consisted largely of bacteria and vibrios. After being well washed, this ferment was placed in a solution of sugar which had been creasoted. Hydrogen and carbonic anhydride were evolved, the sugar was partly inverted, and alcohol, acetic and butyric acids were formed. The ferment was not much changed; the vibrios disappeared, but it contained no torulas, mycelium, or cellules.

II. Starch-paste, treated with the same ferment, rapidly became fluid, with disengagement of hydrogen and carbonic anhydride. Alcohol, acetic, lactic, and butyric acids were formed. In many experiments no glucose could be found; soluble starch or dextrin fermented directly.

III. The granular deposits of old wines invert cane-sugar. They also act as alcoholic ferments. J. T.

Experiments on the Ripening of Grapes. By C. St. Pierre and L. Magnien (*Compt. rend.*, lxxxvi, 491).—The authors find that as the grapes approach maturity, they evolve carbonic acid gas both in the dark and in daylight, this evolution taking place indifferently in air or any inert gas. When the experiment is carried on for a sufficient length of time, the quantity of carbon dioxide produced is always greater than the quantity of oxygen consumed. Grapes absorb or give off moisture according as they are kept in damp or dry places. When maturity approaches, the acids diminish and the sugar increases. The mechanism of ripening, according to the authors, is the following:—The acids and glucose are formed in the plant, and carried by the sap to the grape: here the acids are destroyed, whilst the sugar becomes concentrated. When the grapes become over ripe, the sugar is consumed in its turn. J. M. T.

On Relations between the Chemical Constitution of certain Organic Compounds and their Physiological Importance to Plants. By A. Stutzer (*Landw. Versuchs-Stat.*, xxi, 93—133).—In the first place, experiments were made to determine whether plants containing chlorophyll could obtain their total supply of carbon from oxalic or tartaric acid, instead of carbonic acid. Seeds of *Brassica rapa* were allowed to germinate in distilled water until the radicle and plumules were sufficiently developed; these plants were well suited for the experiment, on account of the small weight of the seed and the rapid growth of the young plant. They were then planted in a bed of sand, under a glass chamber, and watered with a feeding solution—containing ·2 per cent. of Nobbe's feeding-salt—to which freshly-precipitated calcium oxalate had been added. It was found that free acids, or even acid salts, would not answer for the purpose. At the top of the glass chamber two tubes were let in, and one of them connected with an aspirator, by which air freed from carbonic acid (by potassium hydrate) was drawn through. All joints were sealed with paraffin. The vessel was exposed to diffused daylight, except in the early morning when the sun shone on it for a short time. The plants grew well, and were of a good green colour. After 35 days they were removed, washed, and dried at 100°; then weighed. The increase amounted to 228 per cent. Wheat plants treated as above for 30 days gave an increase of 48 per cent.; but as there is a large store of nutriment in this grain, the difference in the increase compared with rape is easily accounted for. Other plants were also found to grow and form new leaves when submitted to the same treatment. On examining the gas, oxygen was found to have been evolved.

Experiments made with calcium tartrate, instead of the oxalate, gave with *Brassica rapa* an increase in weight of 133 to 150 per cent. in 17 days.

The author, therefore, concludes that plants containing chlorophyll can assimilate the carbon from oxalic and tartaric acids.

It was then necessary to determine whether this assimilation of carbon is due to an intermediate formation of carbonic acid, or whether it takes place directly. In the following experiments the air in the chamber was not only freed from carbonic acid at the commencement of the operation, but any carbonic acid that was given off from the plants during the trial was absorbed with potash. *Brassica rapa*, when treated with calcium oxalate under the above conditions, diminished in weight and died. *Poa annua* also lost all its chlorophyll, and finally the plant died. When calcium tartrate was substituted for the oxalate, rape was found to increase in weight during 17 days from 66 to 69 per cent., and a more fully-grown plant of *Viola tricolor* formed new leaves and buds. Carbonic acid was found to have been absorbed by the potash.

Oxalic acid consists of two carboxyl groups, COOH.COOH, and it may be inferred from the above results, that the carboxyl is oxidised into carbonic acid and water before the plant can take up the carbon; whereas the alcoholic groups, (CHOH), contained in tartaric acid can be applied directly to the formation of carbo-hydrates in plants. It has not been determined, however, how this splitting up of the molecule of tartaric acid takes place, but it is most probable that at the moment of separation the COOH-groups become oxidised into CO_2 and H_2O, and do not previously form oxalic acid.

It was found, on comparing these two sets of experiments, that about the same quantity of tartaric acid had been absorbed in each case, but in the latter—with an atmosphere kept constantly free from CO_2—the increase in the weight of the plants amounted to only about one-half of that found in the former instance, when the CO_2 was allowed to remain, and so became finally assimilated. It may, therefore, be taken for granted that the carboxyl group must be oxidised into carbonic acid and water, before plants can take up the carbon; but the alcoholic group, on the contrary, is at once absorbed, without intermediate oxidation.

In experiments on the effect of glycerin on rape—which also contains the CHOH-group—the plants increased 126 per cent. in 17 days, although the air was kept constantly free from CO_2.

Fungi were next grown in solutions containing various salts. It is well known that the fungi do not contain chlorophyll, and as they exhale CO_2, they cannot feed directly upon it; they will behave towards organic compounds, therefore, in the same manner as green plants grown in an atmosphere free from carbonic acid.

Penicillium glaucum was sown in flasks of about two litres' capacity. The feeding solution contained ·2 per cent. of a mixture composed of magnesium sulphate, potassium chloride, and ammonium phosphate. Air was freely admitted, as the mouths of the flasks were only covered with a watch-glass, in order to keep out the dust. They were exposed to diffused daylight. Temperature 15—25°. Pure oxalic acid was added in quantities varying from 1 to 5 grams, and the quantity of feeding solution varied from 1 to 2 litres. In some cases, the oxalic acid was neutralised with ammonia; but even when left for 63 days, no fungoïd growth took place. If, however, other compounds were added containing the CHOH-group—such as glycerin, citric acid, lactic acid, acetic acid, hippuric acid, or succinic acid—there was abundant growth of the fungus. With formic, butyric, and valeric acids, however, no fungoïd growth was produced; this was probably due to their thermo-dynamic relations.

The following were the results finally obtained:—

I. *Carboxyl.*—The fact that the plant cannot take up the carboxyl-group as a direct source of carbon is contradictory to the views of Liebig and Rochleder. They state that oxalic acid is formed from carbonic acid by the plant, thus leading to the formation of other compounds.

II. *Carboxylated Hydrocarbons.*—Some of them can give carbon directly; for instance, acetic and succinic acids. Butyric and valeric acids cannot.

III. *Hydroxylated Hydrocarbons.*—Ethylic alcohol and glycerin can afford a direct source of carbon. Amylic alcohol cannot, however; probably on account of heat relations.

IV. *Carboxylated Hydroxylated Hydrocarbons*, such as lactic, malic, citric, tartatric, and glyceric acids, are especially characterised as furnishing their carbon directly to plants.

V. *Carbonic Oxide and Aldehyde* cannot give carbon.

R. C. W.

On Irrigation with Spring- or River-water. By J. König (*Landw. Versuchs-Stat.*, xx, 185—187).—This paper contains analyses showing the changes in composition exhibited by water which had been used for irrigating a highly siliceous soil. In the winter months this change was but slight, except as regards suspended matters. In summer, however, the diminution of dissolved matters was well marked, and more so in proportion as the temperature was higher.

The author considers it of great importance that water, after being thus used several times, should be exposed to air in order that it may again become charged with oxygen. Ch. B.

On the Silicates of the Shell-Limestone, and their Importance in the Formation of Soils. By G. Weise (*Landw. Versuchs-Stat.*, xxi, 1—17).—This paper contains analyses of the silicates contained in the shell-limestone found in the neighbourhood of Jena. The author regards these silicates as of great importance for agriculture, inasmuch, as by their decomposition under the influence of water containing carbonic acid, they afford large quantities of potash. Ch. B.

Analytical Chemistry.

Detection of Carbon Oxide. By H. W. Vogel (*Deut. Chem. Ges. Ber.*, xi, 235—237).—The author recently published a method of detecting carbon oxide, based upon the change produced by that gas in the absorption-spectrum of blood (*Ber.*, x, 792).

On attempting to detect by this method the presence of carbon oxide in rooms heated by hot air (the unwholesomeness of which has been supposed to be due to carbon oxide), it has been found that the presence of oxygen interferes with the reaction to such an extent, that it cannot be relied upon to indicate small quantities of carbon oxide in such cases. It is suggested that this difficulty might be overcome by absorbing the oxygen, using for this purpose an alkaline solution of ferrous sulphate. But for hygienic purposes it is practically unnecessary to seek to render the test more sensitive; for if the quantity of carbon oxide in the air does not affect the very dilute solution of blood used in this reaction, neither will it affect injuriously the undiluted blood of the lungs. The oxygen present with it is the natural antidote. The author thinks that the harm done by traces of carbon oxide has been over-estimated. At any rate, whatever ill effects may be produced by heating with hot air, they are certainly not due, in many cases, to carbon oxide. J. R.

Volumetric Estimation of Potash. By A. CARNOT (*Compt. rend.*, lxxxvi, 478—481).—The author has already described a method which depends on the precipitation from an alcoholic solution of a double hyposulphite of potash and bismuth (this *Journal*, 1876, ii, 426, and 1877, i, 50; ii, 926). The new method which he now proposes consists in determining the proportion of hyposulphurous acid in an aqueous solution of this double hyposulphite by means of a titrated solution of iodine. On adding the iodine solution to a cold neutral solution of the double hyposulphite, a red precipitate of bismuth oxyiodide is formed, which can be prevented by acidifying with hydrochloric acid, which, in the short time required for the reaction, does not act on the hyposulphite. When the iodine is added, the greenish solution changes to a light golden yellow; towards the end of the operation, however, each drop produces a brownish tinge, which disappears on agitation. The end of the operation is shown by a single drop producing a permanent change from light yellow to dark brown. This change can be clearly perceived either in natural or artificial light. Two equivalents of hyposulphurous acid correspond to one equivalent of potash or of iodine. Details of the preparation of the standard solutions are given, and also the precautions necessary to be observed in conducting the analytical operations. J. M. T.

Notes on Coal Analyses. By T. O. C. SLOANE (*Amer. J. of Sci.* [3], xv, 286—288).—Comparable results in ash determinations can be obtained only when the samples are finely powdered. The fusion method of Fresenius (with salt, nitre, and sodium carbonate) is recommended for sulphur determinations. The specific gravity should always be taken with a tolerably finely powdered sample. The author recommends the use of tracing cloth, instead of glazed paper, for the purposes of sampling and pulverising minerals, coals, &c., for analysis, as it is just as smooth, and much more durable.

M. M. P. M.

Rapid Estimation of Urea. By J. EMERSON-REYNOLDS

(*Phil. Mag.* [5], v, 144—153).—Two instruments are described; the action of both depends on the evolution of nitrogen by the action of sodium hypobromite. In the first instrument the nitrogen is caused to displace its own volume of water from a suitable apparatus, which water is then either weighed or measured. This apparatus is exceedingly simple. In the second apparatus the volume of nitrogen is measured. Neither apparatus can be understood fully without the cuts.

M. M. P. M.

Estimation of Glycerin and Hop-resin in Beer. By V. GRIESSMAYER (*Deut. Chem. Ges. Ber.*, xi, 292—293).—This method depends on the fact that the hop components of beer are soluble in petroleum ether, whilst glycerin is insoluble in it. The operation is conducted as follows:—300 c.c. of beer are evaporated slowly on a water-bath to a third of the volume, and then shaken up with 200 c.c. of petroleum ether; the two layers of liquid, after standing a sufficient length of time, are separated by a tap-funnel, the operation of shaking up with petroleum ether, being repeated with the lower portion. The petroleum ether extract is evaporated on a water-bath, in a weighed basin, dried over sulphuric acid and weighed, thus giving the hop-resin.

The liquid thus freed from the hop components is made alkaline by addition of baryta-water, or better barium alcoholate, and is then shaken up with a double volume of a mixture of 2 parts of alcohol and 3 parts of ether, and the two layers separated. The lower layer is treated as before with the mixture of alcohol and ether. The ethereal extract is heated on a water-bath until all the ether is volatilised, and the residual alcoholic extract is poured in successive portions into a weighed porcelain dish, heated on a water-bath, so that it takes from 15 to 20 hours to reduce it to a viscous fluid, which is then dried over sulphuric acid or phosphoric anhydride for two days, and finally weighed, thus giving the weight of glycerin.

P. P. B.

Estimation of some of the Chief Adulterations of Ground Coffee. By C. KRAUTH (*Deut. Chem. Ges. Ber.*, xi, 277—283).—The author finding that although the presence of chicory and rye can easily be detected qualitatively, yet the microscopic examination of coffee, and the ferric chloride test for chicory, are often unsatisfactory, has submitted several varieties of pure coffee, and the various articles used as means of adulteration, to an examination, the results of which are contained in the following tables:—

(a.) Calculated for 100 parts of the Fresh Substance.

	Different varieties of Coffee roasted.					Chicory roasted.	Chicory un-roasted.	Rye roasted.	Wheat roasted.	Coffee and 10 per cent. rye roasted.	Coffee and 10 per cent. chicory roasted.
	I.	II.	III.	IV.	V.						
Water	1·55	4·37	1·53	1·47	1·57	4·30	6·89	0·28	—	2·15	2·30
Ash	4·43	4·33	4·78	6·29	4·13	10·37	4·99	2·24	2·75	4·22	4·90
Fat	14·45	11·25	13·63	13·33	14·83	1·10	0·41	1·67	1·80	13·80	12·27
Portion soluble in water	24·82	—	—	—	—	62·60	73·29	31·84	52·65	25·39	29·93
Insoluble in water	73·63	—	—	—	—	33·10	19·82	67·88	47·35	72·86	67·77
Sugar	·02	not determined.				22·40	22·20	—	—	0·19	2·25
Sugar after boiling with dilute sulphuric acid	24·21					21·19	not determined	75·16	not determined	28·97	22·62
Ferric oxide obtained by ignition of the ferric chloride precipitate	1·95					1·34	2·03	not determined.			

(b.) Calculated for 100 parts of Dried Substance.

	Different varieties of Coffee roasted.					Chicory roasted.	Chicory un-roasted.	Rye roasted.	Wheat roasted.	Coffee and 10 per cent. rye roasted.	Coffee and 10 per cent. wheat roasted.
	I.	II.	III.	IV.	V.						
Ash	4·49	4·52	4·85	6·38	4·19	10·83	5·35	2·43	1·80	4·31	5·1
Fat	14·78	11·76	13·84	13·53	15·6	1·15	0·43	1·68	2·75	14·16	12·55
Portion soluble in water	25·21	23·51	23·23	22·47	undetermined	65·42	78·71	31·92	52·65	25·98	30·63
Insoluble in water	74·79	76·49	76·77	77·53	undetermined	34·58	21·28	68·07	47·35	74·46	69·36
Sugar	0·20	undetermined				23·40	23·84	—	—	0·19	2·30
Sugar after boiling with dilute sulphuric acid	24·29					22·14	undetermined	75·37	undetermined	29·60	23·15
Ferric oxide obtained by ignition of the ferric chloride precipitate	1·98					1·40	2·17	undetermined.			

The determinations of water, ash, and fat were made in the usual manner; to estimate the part insoluble in water, 30 grams of the material were digested on a water-bath, with 500 c.c. of water, the insoluble portion brought on to a weighed filter, and washed with water, until the filtrate measured 1000 c.c. The residue was then dried at 100° C. and weighed, and from its weight the proportion of soluble matter calculated.

To determine the amount of sugar present, the aqueous extract was evaporated to dryness, the residue extracted with hot alcohol, and after evaporating the alcoholic extract to dryness, the sugar was again dissolved in water, decolorised by animal charcoal, estimated in the usual way, and calculated as cane-sugar.

The determination of "sugar formed by boiling with dilute sulphuric acid" was made as follows:—3 grams of the material were boiled for six or seven hours with 200 c.c. of a dilute sulphuric acid, containing 2½ per cent. acid, the acid removed by addition of lead carbonate, and the whole boiled with animal charcoal for some time. The solution was then made up to 500 c.c. and filtered, and an aliquot part boiled with Fehling's solution; the cuprous oxide so formed was then converted into cupric oxide and weighed, the amount of cane-sugar being calculated from the result.

The iron precipitate was obtained by adding ferric chloride to the aqueous extract; the precipitate was well washed, ignited, and weighed.

The tables show that coffee differs from the substitutes examined, by the large amount of fat contained in it, whilst as regards ash it gives less than chicory, but more than rye or wheat. The differences observed in the proportion of matter soluble in water are still more marked, especially in cases of chicory and wheat. The most marked differences are seen in the numbers showing the amount of sugar contained in the bodies, and that formed by boiling them with sulphuric acid. Thus, whilst coffee scarcely contains any sugar, chicory is seen to contain a large percentage; and the amount of sugar formed by boiling with dilute acid is seen to be characteristic of cereals.

The author thinks that this method of investigation yields not only qualitative results, but may also be made use of to estimate quantitatively the adulteration of ground coffee. P. P. B.

Technical Chemistry.

Bye Products and Waste from the Potash Manufactories of Stassfurt and Leopoldshall, and their Influence on the Land. By T. Pusch (*Dingl. polyt. J.*, ccxxv, 365—367).—The salt deposits have been worked and treated for salt, &c., since the 8th century, but it was not until 1851 that a thorough and efficient system of winning and working was commenced by Carnall.

Whilst sinking the shaft, the abraum salt was found overlying the rock salt, and considered to be worthless. In 1876, 545,396 tons (German) was the output of the salt in Stassfurt and Leopoldshall, and since 1860 4,000,000 tons have been brought to day.

This salt is now treated in 30 works, 20 of them being situated in Leopoldshall, 2 in the adjacent villages of Hecklingen and Gänsefurt, 7 in Stassfurt, and 1 in the Prussian village of Börnicke (*ibid.*, 1875, ccxvii, 388—496; ccxviii, 62).

The waste from these works are the insoluble matters and the mother-liquors, and consist of magnesium chloride, kieserite, sodium chloride, calcium sulphate, besides the waste from Glauber's salt manufacture, which is likewise magnesium chloride. It is reckoned that 180,000 tons of waste pass yearly from these works over the land.

A commission was appointed to examine the surface water, and the table appended is the result:—

In Grams per Litre.

Place from which the samples were taken.	Residue from evaporation.	Lime.	Magnesia.	Sulphuric acid.	Chlorine.	Chlorides of alkalis.	Organic matter and loss.
Above Löderburg	0·850	0·166	0·014	0·196	0·213	0·311	0·108
Below the influx of the coal-pits of Löderburg and Börnicke	1·100	0·166	0·050	0·196	0·390	0·355	0·271
Below the influx streams of the Fabrik Zimmer..	1·425	0·170	0·071	0·208	0·533	0·661	0·192
Behind the pretended salt springs	2·250	0·170	0·066	0·256	0·905	1·526	0·148
Below Forster's and Grüneberg's works........	5·400	0·230	0·400	0·470	2·840	3·800	0·040
260 paces below the influx of the new salt-shaft in the Hirtenwiese	72·110	0·612	1·231	1·120	42·240	69·825	0·430
220 paces below Leissler and Townsend's Works	92·640	trace	5·425	1·304	54·480	80·387	0·432
Mill-stream above the old Royal Salt-shaft	1·695	0·182	0·050	0·260	0·700	1·046	0·118
Mill-stream below the old Royal Salt-shaft	2·480	0·182	0·191	0·256	0·923	1·525	0·147
Boundary stream below the old Royal Salt-shaft	47·750	0·075	6·550	1·128	25·550	29·252	1·253
Leopoldshall, below the island in the Bullenwiese................	4·000	0·200	0·251	0·408	1·562	2·295	0·5093
At the bridge of Hohenerxleben	7·600	0·278	0·580	0·655	3·905	3·326	0·310
At the defences of Neugallersleben	3·550	0·205	0·203	0·384	1·633	1·971	0·478

Close below the discharge drains of the Townsend Fabrik large deposits of kieserite were found.

The analyses show that even above Stassfurt the water is undrinkable, and after passing Stassfurt and Leopoldshall, it cannot even be used for technical purposes. It would be too costly to convey it directly to the Elbe, so that Pusch proposes to let it sink into the land, and to provide fresh water to the inhabitants. S.

Plastilina. By F. GIESEL (*Deut. Chem. Ges. Ber.*, xi, 310).—Plastilina, a proposed substitute for modelling clay, has the following percentage composition:—Fatty acids and fats, 51·2; ZnO, 5·2; S, 30·0; clay, 13·4 per cent.

This substance is best prepared by fusing 343 grams of zinc oleate (obtained by heating 300 grams of oleic acid with 43 grams of zinc oxide) with 130 grams of olive oil and 60 grams of wax; 250 grams of finely powdered sulphur, and 118 of clay are added to the melted mass, and the ingredients are thoroughly incorporated. W. C. W.

Some Thallium Pigments. By T. W. SALTER (*Chem. News*, xxxvii, 96).—This paper, which is unsuitable for abstraction, describes the methods which the author followed in the preparation of the thallium colours, comprising several shades of yellow, orange, red, brown, and green, which were exhibited in the Exhibition of 1871, and of further remarks on their value as pigments. A. J. C.

Seasoning of New Wine Casks (Das Weingrün-machen neuer Fässer). By E. v. BIBRA (*J. pr. Chem.* [2], xvii, 40—42).—A cask is seasoned when wine can be kept in it without losing any of its qualities as a drink. New casks always spoil the first charge, so that it has been the practice to use an inferior wine for the purpose, and then to put in the better class. The author considered that the extractive matters of the wood spoilt the wine, and on instituting experiments in this direction, he found that crystallised sodium carbonate would take up the extractive matters. One pound of soda to a kilderkin of water is sufficient. The process is as follows:—If a kilderkin cask be taken, it is two-thirds filled with spring or river water, and the pound of soda dissolved in water is added. The cask is then shaken for a time, and afterwards filled up to the bunghole, and then allowed to stand for twelve days. The cask has only to be washed out with a little water after the soda has been poured off, to be fit for use. A wine merchant, to whom the author mentioned this method, tried it, and his verdict was, "The wine keeps as well as if it were in glass vessels." S.

Aniline-Black by Means of Vanadium. By F. GOUILLON (*Chem. Centr.*, 1877, 41).—The author recommends for every 100 kilos. of cotton yarn a bath of 150 litres of water, 15 kilos. of aniline hydrochloride, 5 kilos. of potassium chlorate, and 150 grams of a normal solution of 5 grams of ammonium vanadate to a litre of water. After passing through the bath, the goods are hung up for 24 to 48 hours at a temperature of at least 20°. They are then submitted to a very weak bath of potassium bichromate, which produces a pure black colour. A boiling soap-bath is not necessary, but it heightens the colour, and imparts to the fibre a soft, smooth feel. G. T. A.

Resorcin-dyes. By L. DURAND (*Chem. Centr.*, 1877, 76).—Eosin is prepared on a large scale in the following manner:—By passing hot benzene vapours into concentrated sulphuric acid, heated to 240°, benzenedisulphonic acid is obtained (1 part of benzene requires 4 parts of concentrated acid), which is dissolved in the excess of sulphuric acid. The solution is diluted with ten times its volume of water and neutralised with lime, which deposits the free acid as insoluble calcium sulphate, whilst the calcium benzenedisulphonate remains in solution. The mixture is allowed to settle, and the clear liquor is drawn off, and treated with crystallised carbonate of sodium, which converts the lime salt into a soda salt. The solution is filtered and evaporated to dryness. By fusing the soda salt with five times its weight of caustic soda in iron pots provided with mechanical agitators, and heated in an oil-bath at 250°, resorcin is obtained. After heating the melt for 24 to 36 hours, the reaction is finished. The contents of the pot may be poured on cast-iron plates, on which the mass solidifies. The solid is then broken up and dissolved in hot water; whereupon, after neutralising with sulphuric acid and cooling, the greater portion of the sodium sulphate crystallises out, while the resorcin formed remains in solution and is extracted with ether. The ethereal extract leaves on distillation a solid crystalline mass of resorcin. The author prepares phthalic acid by treating pure naphthalene with potassium chlorate and hydrochloric acid, and dissolving the chlorinated compounds in hot petroleum, which deposits a crystalline mass. After removing the petroleum adhering to the crystals with petroleum ether, they are treated with nitric acid, which results in the conversion into phthalic acid. By repeated recrystallisation and final fusion in an oil bath, the pure anhydrous acid is obtained. By fusing a mixture of 2 parts of resorcin with 1 part of phthalic acid at 195—200° till the mixture assumes a thick consistence, fluorescin is obtained, from which eosin may be obtained. The melt is boiled out, in which case all impurities are dissolved, while the residual fluorescin is dried. In order to prepare eosin from it, the bromine-compound must be prepared and converted into a lime salt. The author does not give any data as to the method of preparing this colour commercially.

For printing on cotton, the aqueous solution of eosin is thickened with gum, printed, steamed, and finally passed through a solution of lead acetate, which fixes the eosin to the fibre. Albumin may also be used instead of gum for thickening. In the dyeing of wool, 100 kilos. require 5 kilos. of alum. A fine red colour is obtained with eosin by dissolving 150 grams in one litre, and adding a small quantity of gum senegal. A colouring matter, called *primerose*, is prepared from eosin, which is very suitable for silk dyeing. The author does not give any details as to the preparation of this dye. 1 kilo. of the dye, 12 kilos. of alcohol, and 5 kilos. of water are warmed on a water bath, and mixed with 500 grams of sodium carbonate. In dyeing, soap and acetic acid are added to the bath, and the latter is heated gradually to boiling. After dyeing, the material is well washed, and dried finally.

D. B.

Coloured Printing on Cottons Dyed with Indigo. By J. DÉPIERRE (*Dingl. polyt. J.*, ccxxvii, 96—97).—It is well known that sodium bicarbonate acts upon potassium ferricyanide at the boiling point of water, and that this reaction has been used to discharge the colour from materials dyed with indigo. By printing with a thickened solution of ferricyanide and bicarbonate, and steaming, the blue colour is discharged, and the pattern comes out white. This method has been greatly improved by the author. He has found that a solution of albumin will take up ferricyanide of potassium and sodium bicarbonate, and without any effect being produced on its power of coagulating. He incorporates a mixture of albumin, potassium ferricyanide, sodium bicarbonate, and any colour he wishes to print off, as cinnabar, ultramarine, &c., and prints the required pattern with it. By exposure to steam, the blue indigo colour is discharged, and the albumin with the enclosed colours become fixed. Colours so fixed can be washed both in cold and hot water, and with soap. S.

Chemical Manufactures of Germany at the Centennial Exhibition at Philadelphia, 1876. (*Chem. Centr.*, 1877, 105—121.)

Is Beer containing Buxine to be regarded as Adulterated? By H. HAGER (*Chem. Centr.*, 1877, 119.)

Silicatisation of the Soil. By BREITENLODER (*Chem. Centr.*, 1877, 74.)

Applications of Salicylic Acid in Domestic Economy. By v. HEYDER (*Chem. Centr.*, 1877, 12.)

Casson-Dermoy's Puddling Furnace. (*Dingl. polyt. J.*, ccxxvi, 160.)

Cost of Setting Up a Siemens' Furnace. By P. BARNES (*Dingl. polyt. J.*, ccxxvi, 162.)

Preservation of Meat. By G. JÜDELL (*Dingl. polyt. J.*, ccxxv, 200.)

New Method of Photographic Enlargements. By W. GENTH (*Chem. Centr.*, 1877, 233.)

On the Conditions required in Water intended for Household Use. By F. FISCHER (*Chem. Centr.*, 1877, 264, 280, 300.)

General and Physical Chemistry.

Optical Rotation (1st Communication). By H. LANDOLT (*Liebig's Annalen*, clxxxix, 241—337).—The object of this important research (which has been already noticed in this volume, p. 1) is to trace the variations in the rotatory power of an active substance when certain definite changes take place in its chemical composition. The author gives an exhaustive sketch of the work previously done in this direction, and also an account of his own investigations.

GENERAL PART.—Active bodies are divisible into three classes:—

(1.) *Those which are active only in the Crystalline Form, losing this Property when fused or dissolved in an Inactive Liquid.*—These are either single-refracting or uniaxial double-refracting crystals, whose rotatory power depends entirely on the crystalline or molecular structure, and belongs therefore to the domain of physics.

(2.) *Those which are active only in an Amorphous Condition (fused or in solution).*—These are carbon compounds occurring in plants or animals, or derivatives of them: some bodies of this class, however, have been produced synthetically. Substances of this class, such as camphor, have no rotatory power in the crystalline state, the crystals being biaxial (*vide supra*), although, as in the case of sugar which has been fused, they retain that power in the solid amorphous condition.

(3.) *Those which are active both in the Crystalline State and in Solution.*—Only two members of this class are at present known, viz., hydrated strychnine sulphate (quadratic octahedrons) and amylamine alum (regular).

The activity of the members of the second class is a property of the molecules, and depends on the arrangement of the atoms therein, as is also conclusively shown by the fact that turpentine oil and camphor (Biot, *Mém. d. l'Acad.*, ii, 114; *Gernez. Ann. Scient. d. l'Ecole. Norm. Sup.*, i, 1) possess the same rotatory power in the gaseous and liquid states. The phenomenon in this case therefore belongs to the domain of chemistry. The cause of the optical activity in crystals and in liquids being essentially different, Biot has applied to the latter the term *molecular rotation.*

According to Pasteur (*Recherches*, p. 27) molecules are divisible into two classes: (1.) Those in which the atoms are symmetrically arranged. (2.) Those in which the arrangement is unsymmetrical. The property of optical activity belongs to the latter class only, and Le Bel has proposed the hypothesis, that when a carbon atom is united with four different radicles, an unsymmetrical form of molecule is produced, which must therefore be optically active. This view is supported by Van t'Hoff, who finds, from a comparison of the chemical composition of all known active and many inactive bodies, that none of those possess rotatory power in which asymmetrical carbon atoms are wanting. Moreover, active bodies always contain one or more asymmetrical carbon atoms, an asymmetrical carbon atom being one which is united with unlike simple or compound radicles.

These facts will be of considerable service in controlling the determination of structural formulæ.

Specific Rotatory Power.—The specific rotatory power $[\alpha] = \frac{a}{l.d}$, where $d =$ density and $l =$ length of the column of the substance through which the ray passes. If the density is referred to that of water at 4° C., it expresses the weight of 1 c.c., and the specific rotation can therefore be considered as the rotation which 1 gram of active substance produces when it occupies the space of 1 c.c., and when a column 1 decim. long acts on the ray. Since the temperature influences l and d, the temperature at which the determinations are made must be stated: for although the specific rotatory power of a pure substance is constant for the same temperature, it varies with the temperature.

The specific rotatory power of a solid dissolved in an inactive indifferent solvent, is determined as follows: If P grams of active substance be dissolved in E grams of inactive solvent, and if d be the density of the solution, then 1 c.c. of the latter contains $\frac{P}{P+E}d$ grams of the active body. If the angle of rotation for a column of this liquid 1 decim. long is α, then for a liquid which contains 1 gram of active substance in 1 c.c., *i.e.*, the specific rotation, $[\alpha] = \frac{\alpha(P+E)}{l.P.d.}$. If $\frac{P}{P+E}$ (*i.e.*, amount of active substance in the unit-weight of solution) $= \epsilon$, then $[\alpha] = \frac{a}{l.\epsilon.d}$, and if p represents the percentage composition of the solution by weight, then $[\alpha] = \frac{\alpha \cdot 100}{l.d.p.}$, and $p.d = c$, the concentration (*i.e.*, the number of grams of active substance in 100 c.c. of the solution).

Until recently it has been customary to neglect the determination of the density of the solution, a weighed quantity of the active body being dissolved in a flask of known volume, and diluted to the mark, but in many cases this is insufficient; for the specific rotation of bodies in solution is not constant, but varies more or less with the quantity of inactive liquid, the influence of which may be calculated when the percentage composition of the liquid is known, but which is not possible when only the concentration has been determined; it is therefore necessary to know the density also.

Biot in his earlier experiments found that, with the exception of tartaric acid, the rotation was proportional to the quantity of active substance in solution, when the columns were of equal length, and therefore the same value was obtained for $[\alpha]$ whatever the concentration of the liquid. In 1852, however, he proved that other substances besides tartaric acid did not obey this rule, and also that the nature of the solvent exercised considerable influence. He concluded, therefore, that the specific rotation derived from solutions is not a constant number, and that circular polarisation could no longer be considered as a result of a simple mechanical distribution of active molecules in an optically indifferent medium.

These facts, however, remained for a long time without notice, and specific rotatory powers were still determined without reference to the concentration or to the nature of the solvent.

Oudemanns (*Pogg. Ann.*, cxlviii, 337) and Hesse (*Liebig's Annalen*, clxxvi, 89, 189) have recently made numerous determinations of rotatory powers with solutions of different degrees of concentration, which prove that with a small variation in the latter, almost all bodies show an essential variation in their specific rotation. Still greater differences occur when the solvent is varied.

Biot some time ago (*Mém. d. l'Acad.*, xv, 205; xvi, 254), however, pointed out a means by which this method might be utilized for the determination of the specific rotatory power. The specific rotation of an active liquid may be determined directly, and is a constant number for a given temperature. If such a body be now mixed in different proportions with an inactive liquid, and the specific rotation calculated from the composition, density, and angle of rotation, values are obtained which differ more or less from that found for the pure substance. If now this variation be represented by a curve so that the abscissæ indicate the percentage amount of inactive solvent, and the ordinates the corresponding values for $[\alpha]$, we have a method for finding the specific rotation of the pure substance. For when the curve is a straight line we have the equation—

$$\text{(I.)}\ [\alpha] = A + Bq;\ \text{if it is not}$$
$$\text{(II.)}\ [\alpha] = A + Bq + Cq^2.$$

Here A expresses the specific rotatory power of the pure substance; B and C the increase or decrease which A suffers through the influence of 1 per cent. of inactive solvent, and q the percentage amount of inactive solvent.

With liquid active bodies, which mix in all proportions with an indifferent liquid, the changes which the specific rotation undergoes may be ascertained from $q = 0$ to $q = 100$, and a complete curve constructed.

If A be calculated from the results obtained with a number of solutions, a value will be found agreeing more nearly with the actual specific rotation the greater the portion of the curve included. If the active body is solid, its original specific rotation cannot be determined directly, but a curve may be obtained which will approach more or less the point where $q = 0$, and values may be calculated for B and C which may serve by extrapolation for the determination of the specific rotation of the pure substance. This method is applicable with safety only when the changes are represented by a straight line, or where a large portion of the curve has been determined directly, the latter depending on the solubility of the active body in the indifferent liquid.

In the case of a mixed solvent the process is far more complicated, but in many cases, notwithstanding, the specific rotation may be found by an extension of the above method.

The author explains the influence of the inactive solvent as follows:—

If between the molecules of an active substance, which all exercise an equal attraction on one another, other molecules are introduced the attraction of which is different, a certain modification in the structure of the active body is produced, and in such a way that the arrangement of the atoms in space, as well as the nature of the atomic movement, suffers a change, which is greater the larger the number of inactive molecules present.

SPECIAL PART.—In this section of the memoir the author describes the experiments he has made to prove that the method of determining the specific rotation of a pure substance, according to the interpolation method, gives correct results.

For measuring the angle of rotation in these investigations he employed—

(1.) Two Wild's polaristrobometers, graduated through 360° and capable of being read off to 1′. To eliminate errors as far as possible, the observations were repeated five times in each of the *four* quarters with full and empty tubes.

(2.) A Mitscherlich's polarisation apparatus, which could be used with tubes 1 meter long. As a source of light, a sodium flame produced by a vertical gas blowpipe was employed, the green and blue rays being cut off by bichromate solution.

(3.) A Laurent's polaristrobometer, illumined by the sodium flame, in which the zero point corresponds to the equal illumination of the two halves of the circle of light (*Compt. rend.*, lxxviii, 349).

In order to avoid any error due to variation of temperature in the liquids examined, each observation tube was surrounded by another, through which a stream of water at 20°C. was allowed to flow. The tubes holding the liquid were closed in the ordinary manner with glass plates, but as many samples of glass produce circular polarisation (Scheibler, *Ber.*, i, 268), all the glass covers employed were subjected to a careful investigation. The length of the observation tube was measured in the following way:—A glass tube closed at one end, and a few mm. shorter than the observation tube, was taken, and a thick pointed glass rod fitted into it by means of a piece of caoutchouc tubing, so that the one could slide in the other without much friction. It was then placed in the observation tube, which was closed by pressing down the glass cover. On carefully withdrawing the tube and rod and measuring it by means of a cathetometer, the length of the interior of the observation tube could be ascertained with great accuracy.

The different polarisation instruments were compared by observations with solutions of sugar, and with a mixture of negative turpentine oil and alcohol. A difference in the angle of rotation occurred only in the second place of decimals. The balances and weights employed were previously subjected to a rigid examination; and all the weighings made with the greatest care. In all cases the weights obtained were reduced to a vacuum.

In making up the solutions, the active substance was first weighed out into a stoppered flask, and the solvent added in the desired proportion, the exact weight of the latter being taken.

The specific gravity of the liquids was determined at 20°; repeated determinations with the same substance showed that differences occurred only in the fifth decimal place.

The graduation of the measuring flasks was conducted in the ordinary manner described by Mohr, 100 grams of water at 17·5° being taken as 100 c.c., the specific gravity of the liquid being referred to water at 17·5°. The value of the concentration of the solutions and of the specific rotation was, therefore, different from that obtained by the use of true c.c. In practical saccharimetry, where flasks graduated at 17·5° are used for preparing the solution, the rotation-constant of sugar is referred to Mohr's c.c., whilst in scientific investigations the true c.c. must be taken as the basis. The neglect of this point in treatises on specific rotation has led to considerable differences, Mohr's c.c. (at 17·5°) giving a result about 0·12 per cent. less than the true c.c. (at 4°). The reduction of the weighings to a vacuum causes a difference only in the third decimal place.

In the author's observations the values for the percentage composition, concentration, specific gravity, and specific rotation are always referred to true c.c., and the reduction of the weighings to a vacuum. To convert them into Mohr's c.c., it is only necessary to divide by 1·00125.

In order to ascertain how far the specific rotation of a body can be ascertained from that of its solutions, the author has determined and compared the specific rotation $[\alpha]_D$ of positive and negative turpentine oil, nicotine, and ethyl tartrate, both in the pure state, and mixed with various inactive liquids (water, alcohol, benzene, and wood-spirit), according to Biot's method. The formula given corresponds with the whole of the curve representing the experimental determinations from the most concentrated to the weakest solutions, and as these begin with mixtures which contained at least 90 per cent. of active substance, the constant A differed but little from the real value.

Results.—(1.) On increased dilution with an indifferent liquid, the specific rotation does not undergo a sudden, but a gradual change. Whether it increases or decreases, however, depends on the nature of the active substance: thus, turpentine and ethyl tartrate, when mixed with various solvents, always show an increase, whilst nicotine and camphor show a decrease in the specific rotation. Equal increments of different solvents act on one and the same substance unequally; so that where these changes are represented graphically, a different curve is obtained for each solvent, starting from the point which represents the rotation of the pure substance. The following table gives the difference between the values for $[\alpha]_D$ when $q = 0$ (pure substance) and $q = 100$ (maximum dilution).

Active substance.	Solvent.	$[\alpha]_D$ $q = 0$.	$[\alpha]_D$ $q = 100$.	Difference.
− Turpentine	Alcohol	36·97	38·79	+ 1·82
	Benzene	36·97	39·79	+ 2·82
	Acetic acid	36·89	40·72	+ 3·83
+ Turpentine	Alcohol	14·17	15·35	+ 1·18
− Nicotine..........	Alcohol	160·83	138·59	−22·24
	Water	161·29	74·13	−87·16
+ Ethyl tartrate	Alcohol	8·27	10·19	+ 1·92
	Wood spirit....	8·42	11·19	+ 2·77
	Water	8·09	28·12	+20·03

(2.) From the rotatory power of a number of its solutions, that of the pure substance may be calculated; the accuracy with which this can be done depending on the amount of change produced by the inactive liquid, and whether the curve representing this change is a straight line or is more or less curved. The more concentrated the solution also, the more accurate will be the calculated result. When the equation $[\alpha] = A + Bq$ is used, the calculated value of A agrees sufficiently well with the specific rotation of the pure substance when the most concentrated solution contains about 50 per cent. of the active body. When the formula $[\alpha] = A + Bq + Cq^2$ has to be employed, it is necessary that the solutions should not contain less than 80 per cent.

(3.) The same value is always obtained for the specific rotation of the pure substance, whatever the indifferent solvent used. The results with ethyl tartrate, for example, are:—

		Difference.
Direct observation .... $[\alpha]_D$	$=8·31$	—
Calculated for mixtures with alcohol	$=8·27$	−0·04
” ” wood spirit	$=8·42$	+0·11
” ” water	$=8·09$	−0·22

In determining the specific rotation as above described, the solutions should be as concentrated as possible, and since the nature of the solvent does not influence the result, it should be chosen with this object.

With Equation (I), at least three solutions of different strengths should be prepared, and their specific rotation determined. In the case where Equation (II) has to be employed, more than three solutions must be investigated. No method is at present known by which the specific rotation of difficultly-soluble substances can be determined. By the above methods the author has determined the specific rotation of a *solid* body, viz., camphor (b.p. 204, m.p. 175), with the following results:—

Solvent.	$[\alpha]_D$ for $q = 0$. Pure substance.	$[\alpha]_D$ for $q = 100$. Infinite dilution.	Difference.
Acetic acid	55·5	41·8	13·7
Acetic ether	55·2	50·8	4·4
Monochloracetic ether	55·7	49·0	6·7
Benzene	55·2	38·9	16·3
Dimethylaniline	55·8	40·9	14·9
Methyl alcohol	56·2	45·3	10·9
Ethyl alcohol	54·4	41·9	12·5

Mean specific rotation of pure camphor at 20° ...... $[\alpha]_D$ = 55·4

Mean deviation .... = ± 0·4

The only non-crystalline solid substances, besides camphor, of which the specific rotation in the pure state is at present known, are grape-sugar and cane-sugar, which have been determined by Tollens (*Deut. Chem. Ges. Ber.*, ix, 1531; x, 1403); and cane-sugar and tartaric acid by Biot (*Ann. Chim. Phys.* [3], x, 175; xxviii, 351). T. C.

A Simple Method of Observing the Reversed Lines of Spectra. By C. GÜNTHER (*Ann. Phys. Chem.* [2], ii, 477).—A fine platinum wire held vertically in the outer flame of a Bunsen's burner serves at once as source of light and as a slit, when viewed across the flame through a prism. A sodium compound introduced into the intervening part of the flame would ordinarily exhibit the monochromatic spectrum of sodium; but now the spectrum of the glowing wire behind causes the reversal of the D line, which therefore appears dark. Similar phenomena occur with other metals. R. R.

Grove's Gas Battery. By H. F. MORLEY (*Phil. Mag.* [5], v, 272—281).—The author's experiments show that at least a part of the current in the gas battery is due to dissolved gases. By arranging a battery with plates wholly immersed, and raising these until the platinum cuts the surface, it is shown that the increase of current consequent thereupon is too small to necessitate the assumption that a new force is thereby brought into action. Strength of current suddenly falls when resistance is suddenly increased, but it rises again to nearly its former value. So when resistance is diminished, the current rises suddenly, but afterwards falls to nearly its former value. In the first case the diminished current causes a diminution in the amount of gas used, the electromotive force, and therefore the current, being thus raised. In the second case the increased current uses more gas; the electromotive force is therefore diminished, and the current falls. It is further shown that the current is directly as the pressure. This seems to prove that there is really no antagonistic force kept up by hydrogen attached to the positive wire, as supposed by Gaugain.

M. M. P. M.

Galvanic Current between Solutions of the same Substance of different Degrees of Concentration. By J. MOSER (*Ann.

Phys. Chem. [2], iii, 216—219).—The author finds that in a couple formed by the same liquid of different degrees of concentration, a current passes from the more dilute to the more concentrated solution, the liquids being in separate vessels connected by means of a syphon, and having a metallic plate in each. This current was observed with zinc and sulphuric acid, with zinc sulphate, nitrate, chloride, and acetate, with copper sulphate and nitrate, iron chloride, silver acetate and nitrate, &c. The electromotive force, however, is but feeble, the largest observed being only ·027 of that of a Daniell—as estimated by Du Bois-Reymond's modification of Poggendorff's compensation method—in a couple consisting of a solution containing 30 parts of $CuSO_4,5H_2O$ in 100 of water, and the same diluted with 29 times its volume of water. In this form of couple the metal is dissolved by the more dilute solution, and deposited from the more concentrated. C. E. G.

Electrical Conduction and Electrolysis of Chemical Compounds. By L. BLEEKRODE (*Ann. Phys. Chem.* [2], iii, 161—196).—According to Hittorf, the resistance of a compound to electrolysis depends upon the difficulty with which the molecules exchange their constituents. The author has endeavoured to test this theory, and also to ascertain whether the presence in a compound of hydrogen which can be replaced by metals or radicles is connected with its capacity for being electrolysed. The substances examined were in the liquid state—condensed when necessary by pressure—and never in solution. They were contained in narrow glass tubes, the electrodes being platinum wires a few millimeters apart. The current was obtained from batteries of 20, 40, and 80 Bunsen's cells respectively, and finally from De la Rue's chloride of silver battery of 8,040 cells.

According to the above hypothesis, those substances which have very active chemical properties, or which easily give up their hydrogen, should be easily electrolysed. But the results of this investigation in no way bore this out. For instance, besides water and alcohol, which were already known to be very doubtful conductors when pure, the liquid hydrogen acids, such as HCl, H_2S, &c., possess very feeble conducting power. HCN forms an exception to this group, being a good conductor. It should be mentioned, however, that these acids in the pure liquid state are not very active in their chemical properties. The organic metallic compounds, although very unstable, are amongst the worst conductors known.

On the other hand, the anhydrides of the metals are both chemically active and conduct electrolytically, so far supporting Hittorf's hypothesis. Many other substances were examined, some of which gave results in accordance with, and others at variance with the hypothesis. The amines, amides, and hydrocarbons showed no correspondence between their chemical properties and conductivity. Some organic compounds, C_2N_2, CS_2, &c., showed no conducting power. Nothing definite was ascertained as to the function of hydrogen, although all the conductors either contained hydrogen or a metal.

With De la Rue's battery, although some of the substances still showed no trace of electrolysis, they seemed to be affected, as there was a sort of undulatory motion of the surface of the liquid.

The author remarks that his experiments have shown ammonia and hydrocyanic acid to be good electrolytic conductors at ordinary temperatures, the only known cases of pure liquids acting thus.

J. H. P.

Numerical Value of the Constants in Weber's Formula. By W. VOIGT (*Ann. Phys. Chem.* [2], ii, 476—477).—A mathematical paper, proving that the ratio between the mechanical unit and the electro-magnetic unit is 1 : 155570·10^6 instead of 1 : 155370·10^6; and that the constant C of Weber's formula is 440010·10^6 Mm instead of 439450·10_6 Mn.

R. R.

Some Properties of Alloys. By E. WIEDEMANN (*Ann. Phys. Chem.* [2], iii, 237—250).—I.—*On the Expansion and Rate of Cooling of Rose's and Lipowitz's Alloys.*—Ermann found that the specific gravity of Rose's metal diminished with rise of temperature, but increased again immediately before fusion. These results were confirmed by Kopp; and more recently W. Spring has determined the changes in volume due to rise of temperature in Rose's, Darcet's, Wood's, and Lipowitz's alloys. The compositions of these alloys are—

	Sn.	Bi.	Pb.	Cd.
Rose.........	43·55	49·00	27·54	—
Darcet.......	21·26	49·25	27·55	—
Wood.........	13·73	55·74	13·73	16·80
Lipowitz.....	12·76	49·98	26·88	10·38

The author describes the apparatus used by Spring, and points out that with it the observers studied only the phenomena during the heating of the metal, while in his (the author's) opinion the observation of phenomena during the cooling of the metal are of equal importance in answering the question, whether or not the irregular expansion may be due to different modifications or molecular conditions of the alloy.

Wiedemann in his experiments uses a small cylinder of the alloy, which is placed in a test-tube, and the whole is introduced into a glass tube, terminating at one end in a capillary tube about 1½ meters long, from which a lateral tube with a stop-cock is made to project. The lower end of the glass tube is finally closed before the blowpipe. The lateral tube passes to the bottom of a Woulff's bottle filled with oil, and having its other opening connected with an air-pump. Both parts of the apparatus are placed in water-baths and thoroughly exhausted; then by allowing air to enter the pump the oil is forced into the dilatometer, the stop-cock is then closed, and the receding of the oil is observed at intervals representing 5° of temperature.

In the case of Rose's alloy, contraction of the metal took place on cooling from 100° to 90°, when it solidified; on cooling to 50° sudden and considerable expansion took place; but in some cases this happened at 70°, when it was slower and more regular. When the expansion has reached its maximum, continued cooling produces contraction. The same phenomena occur in the inverse order on reheating the metal. The temperature at which contraction takes place on heating is higher than that at which expansion takes place on cooling. When the metal, instead of being fused a second time, was only heated to 85°, the same phenomena took place on cooling, but with greater regularity. The author points out that the circumstance that it takes hours and sometimes days for the contraction or expansion to be completed, goes far to show that in these cases it is not ordinary expansion but a molecular change which is taking place. Rapid heating and cooling between 20° and 88° produce much larger expansions and contractions than when the changes in temperature take place slowly. Wiedemann explains the phenomena by assuming two modifications of the metal α and β, the first stable at low, the second at high temperatures. When α is heated rapidly, it has not time to change until it reaches a comparatively high temperature, when the change to β takes place suddenly; whilst similar changes take place during the cooling of the β modification. Lipowitz's metal gave the same results, although the changes are not so great.

The author further examined the rate of cooling of the two metals by means of a thermal element of German silver and iron, and a mirror galvanometer, and gives a table of the results. He points out that they do not lead to any definite conclusion as to the specific heat of the metals, as the molecular modifications take place between wide intervals of temperature.

II. *Alloys having more than one Melting Point.*—Differing from the conclusions drawn by Rudberg (*Pogg. Ann.*, xviii, 240) from his experiments on the cooling of fused alloys of tin and lead, and tin and zinc as to the double melting point, Wiedemann has repeated them, and gives his results in a tabular form. The alloys experimented on were lead-tin (SnPb) and tin-zinc (Sn_6Zn); he also used tin alone as a check. The author points out that his results show that no real constant temperature for either of the alloys is found above 182° for one and 197° for the other, but that at about 250° the cooling suddenly becomes much slower, again becoming more rapid on approaching the first-mentioned temperatures. After remaining constant at these temperatures for some time, the thermometer again fell more and more slowly until the alloy attained the surrounding temperature. This may be explained by the supposition that the alloy dissolves the excess of metal in larger quantities as the temperature rises, in the same manner as a solvent dissolves larger quantities of a salt with increase of temperature. The so-called second melting point of alloys, therefore, the author considers, is really the point at which a metal dissolved in the alloy begins to be deposited on cooling.

On the Specific Heats of Amalgams.—Regnault found that the specific heats of alloys is equal to the mean of the specific heats of their components; exceptions to this rule exist in certain Bi, Sn, Pb alloys, and Spring has since shown that certain Cd, Sn, Pb, Bi alloys and amalgams also do not conform to the above rule. In the case of the former these differences may probably be explained by the occurrence of molecular changes, accompanied by evolution of heat. The case of the amalgams would appear to be similar to the tin-lead alloys above 182°, viz., that they are a mixture of a solid and a fluid, the proportions of which vary with the temperature. To prove this, two amalgams, SnHg and Sn_2Hg, were examined with tin as a comparison, the results of which are given in a tabular form. At high temperatures both amalgams cooled nearly as rapidly as the tin, showing the specific heats of the tin and its two amalgams to be nearly the same, which would be the case if it is assumed that the specific heats of alloys are the mean of that of their components. SnHg at 128° and Sn_2Hg at 164° behave in the same manner as the tin-lead alloys in the neighbourhood of the so-called second melting point; but the temperature does not appear to remain constant for any length of time at any fixed point, as it did for seven minutes in the case of the tin-lead alloy.

J. M. T.

On the Temperature of Flame. By F. Rossetti (*Gazzetta chimica italiana*, vii, 422—429).—As the air thermometer is evidently inapplicable to the measurement of the temperature of flame, and the use of Siemens' electrical pyrometer for the purpose presents great difficulties, the author had recourse to a thermoelectric pile, consisting of a thin platinum wire and an iron one, both surrounded by porcelain. The results obtained with this instrument, at temperatures below 825°, were carefully determined, and a curve constructed which, as it was but slightly curved for high temperatures, could be prolonged without fear of introducing any considerable error into the observations.

By this method the author has ascertained the temperature of the flame of the Bunsen burner, and finds that the external pale-coloured layer of the luminous shell is about 1350°, the violet-coloured layer immediately beneath this about 1250°, and the bright blue layer immediately surrounding the obscure nucleus about 1200°. The temperature of the obscure nucleus varies greatly in different parts (from 250° to 650° about).

The temperature of the non-luminous flame produced by the combustion of a mixture of carbonic anhydride and coal-gas was also determined. In this case the flame appears to consist merely of one outer luminous layer, and a non-luminous nucleus. With 2 vols. of gas and 1 vol. of CO_2, the temperature at the vertex of the flame was about 1000°; with 1 vol. gas to 2 vols. CO_2, about 860°; whilst with 1 vol. gas to 3 vols. CO_2, it was only 780°. This shows conclusively that the absence of luminosity in a flame of this character is due in great part at least to the cooling effect of the inert gas. In the same way it was found that the introduction of a larger quantity of air into the flame of a Bunsen burner lowered its temperature considerably.

C. E. G.

Use of Oil-Gas for Gas Blowpipes. By O. Lohse (*Ann. Phys. Chem.* [2], ii, 479).—The author recommends the use of oil-gas for the gas blowpipes in laboratories, and finds that it gives a higher temperature than coal-gas.

R. R.

Molecular Constitution of Vapours. By A. Naumann (*Deut. Chem. Ges. Ber.*, xi, 429—431).—A controversial paper, in which the author, replying to Horstmann (*Ber.*, xi, 204), shows that by his distillation-method, the molecular weights rather than the vapour-densities of bodies are determined. The discrepancies between the results of their respective determinations of the vapour-density of acetic acid (*Ber.*, iii, 78 and 702), he refers to the impurity of the acid (m. p. 14°) employed by Horstmann: hence the omission of any mention by the author of certain of the latter's results.

C. F. C.

Relation between the Atomic Weights of the Elements. By F. WAECHTER (*Deut. Chem. Ges. Ber.*, xi, 11—16).—The author has arranged 29 of the elements in a table, from which it appears that analogous elements, such as H, Cl, Br, and I, for instance, or N, P, As, and Sb differ in atomic weight by 16, or some multiple of 16 (approximately).

Quantivalence.	*a*.	*a* + 16.	*a* + 2 × 16.
Univalent	Fl, 18·96	Cl, 35·46	—
Bivalent	O, 16·00	S, 31·98	—
Trivalent	N, 14·04	P, 31·05	—
Quadrivalent	C, 11·97	Si, 28·05	—
Trivalent	Bo, 10·80	Al, 27·48	Y, 46·20
Bivalent	G, 9·30	Mg, 24·38	Ca, 39·97
Univalent	Li, 7·02	Na, 23·04	K, 39·12

Quantivalence.	*a* + 4 × 16.	*a* + 5 × 16.	*a* + 7 × 16.	*a* + 8 × 16.
Univalent	Br, 79·95	—	I, 126·85	—
Bivalent	Se, 79·43	—	Te, 128·00	—
Trivalent	As, 74·91	—	Sb, 122·27	—
Quadrivalent	—	—	—	—
Trivalent	—	Ce, 92·50	—	Di, 138·10
Bivalent	—	Sr, 87·51	—	Ba, 137·17
Univalent	—	Rb, 85·36	—	Cs, 133·04

The author finds, moreover, according to this arrangement:—

1. That the chemical affinity of the elements from fluorine to silicium decreases with the atomic weight and with the quantivalence, whilst from silicium to cæsium it increases.

2. The mean of the atomic weights of any two elements with equal but opposite chemical affinities is nearly the same, namely, 76.

3. The melting and boiling points of the elements, as far as is known, increase from fluorine to silicium, and decrease from silicium to cæsium.

4. The specific heat in the solid state decreases as the atomic weight and quantivalence increase.

5. The density of the elements (in the same vertical column) in the solid state is greater the higher the quantivalence.

6. The affinity of the negative metalloïds (fluorine to silicium) for the metals increases as the atomic weight and quantivalence become higher.

C. E. G.

Imperviousness of the Adjusting Materials of Air-Pumps to Aqueous Vapour. By H. LASPEYRES (*Ann. Phys. Chem.* [2], ii, 478).—The author has assured himself that no transpiration of aqueous vapour takes place through the layers of fatty substances used in the adjustments of a good air-pump. R. R.

Inorganic Chemistry.

Action of Ozone on Iodine. By M. J. OZIER (*Compt. rend.*, lxxxvi, 722).—By passing the electric discharge continuously through a tube containing oxygen and the vapour of iodine, the author has determined the formation of periodic acid, in addition to lower oxides of iodine. C. F. C.

Determination of Nitrous and Nitric Acids. By G. LUNGE (*Deut. Chem. Ges. Ber.*, xi, 434—441).—The author first discusses the reasons for preferring the ferrous sulphate method, in the modified form proposed by himself, to those methods in use for the determination of nitrous and nitric acids, which require the employment of permanganate.

He then figures and describes a much simplified form of the apparatus invented by Davis (*Chem. News*, xxxvii, 45) for the estimation of these acids by Watts' method, *i.e.*, by measurement of the nitric oxide evolved by the action of concentrated sulphuric acid in presence of mercury. This modification, which resembles Rault's gas-burette (as modified by Bunte), consists of a graduated burette, furnished with a stopcock and funnel at the upper end, the lower end being in communication with a similar non-graduated tube by means of a caoutchouc tube, thus dispensing with Davis's mercury trough; moreover, it admits of being much more rapidly cleaned than the original form. For details of manipulation, &c., the author's paper should be consulted. In conclusion the results of a series of determinations are given, which prove that the accuracy of this method is in no way impaired by the presence of arsenious acid, glucose, and other oxidisable substances. C. F. C.

Persulphuric Oxide, a new Oxide of Sulphur. By BERTHELOT (*Compt. rend.*, lxxxvi, 20—26).—*Formation.*—Persulphuric oxide is produced by the action of an electric discharge of high tension on a mixture of equal volumes of sulphurous oxide and oxygen in a state of perfect dryness; also by the cautious addition of hydrogen dioxide to concentrated sulphuric acid, and by the electrolysis of the latter. It is formed probably in many cases by the action, at a low temperature, of metallic peroxides and other oxidising agents on concentrated sulphuric acid.

Preparation.—Persulphuric oxide is prepared by means of the author's concentric tube apparatus (*Ann. Chim. Phys.* [5], xii, 463). After about eight or ten hours, the surface of the annular space becomes covered with oily drops, or with a thin, iridescent layer, either of which, exposed to a temperature of about zero, crystallises in indistinct, granular crystals, or in thin, transparent, flexible needles several centimeters long and of perceptible width, some of which extend across the tube, whilst others remain fixed to the sides, and grouped in tufts. The crystals have a vapour-tension of several centimeters at 10°, and sublime easily.

Composition.—After the reaction is terminated, the residual gas is extracted, measured, and analysed. If the reaction has been complete, the residual gas consists entirely of oxygen, and occupies one-eighth of the volume of the original mixture; that is, two molecules of sulphur dioxide unite with three atoms of oxygen, to form persulphuric oxide, according to the equation, $2SO_2 + 3O = S_2O_7$. The direct analysis of the product may be made by causing it to act on a known quantity of stannous chloride, and afterwards estimating the residual stannous salt by means of permanganate; the sulphuric acid formed may also be estimated as barium sulphate. Two analyses gave the following results:—

Sulphur trioxide.	Excess of oxygen.	Proportion.
83·4	8·23	10·1
94·1	10·00	9·4
Theory, 80·0	8·00	10·0

These analyses were verified by various other methods.

Persulphuric oxide may be kept for some days at a temperature of about 0°, but it decomposes spontaneously after a time. Its aqueous solution decomposes rapidly; the solution in concentrated sulphuric acid slowly evolves oxygen, and is completely decomposed in about six weeks.

Persulphuric oxide is immediately decomposed by heat; and in contact with moist air, it gives off thick white fumes, consisting of ordinary sulphuric acid.

The solution of persulphuric oxide in ordinary sulphuric acid may be diluted without decomposition, even after 24 hours. But on keeping, it gives off oxygen, and that more quickly in contact with spongy platinum, or by the application of heat. Persulphuric oxide alone oxidises sulphur dioxide to trioxide, $S_2O_7 + SO_2 = 3SO_3$; but if the persulphuric oxide is dissolved in a large quantity of sulphuric acid, hyposulphuric oxide is produced, $S_2O_7 + 2SO_2 = S_2O_5 + 2SO_3$.

Persulphuric oxide dissolves in water, and for the most part decomposes. About one-fifth, however, remains combined, and may be estimated by iodide of potassium. The presence of a large excess of sulphuric acid gives greater stability to the compound.

Baryta-water produces an analogous effect, barium sulphate being precipitated, and a small quantity of barium persulphate remaining dissolved, decomposing slowly into barium sulphate, sulphuric acid, and oxygen. Barium persulphate has probably the formula, BaS_2O_8; it could not be obtained in the solid state.

Persulphuric oxide in the cold oxidises sulphurous acid, potassium iodide, ferrous sulphate, and stannous chloride; but it has no effect on arsenious or oxalic acid, in which respect it resembles hydrogen dioxide; it differs, however, from the latter in not forming perchromic acid, and in not decomposing potassium permanganate. It can exist in solution with hydrogen dioxide, also with ozone in the anhydrous or dissolved state.

Persulphuric oxide is the seventh term of the series of sulphur oxides, of which the following are the names and formulæ:—

S_2O unknown; analogous to Cu_2O.
S_2O_2 hyposulphurous oxide.
S_2O_3 unknown; analogous to Mn_2O_3.
S_2O_4 sulphurous oxide.
S_2O_5 hyposulphuric oxide.
S_2O_6 sulphuric oxide.
S_2O_7 persulphuric oxide.
S_2O_8 unknown; analogous to Os_2O_8.

C. W. W.

Preparation of Potassium Nitrite. By PERSOZ (*Chem. Centr.*, 1878, 157).—Metallic copper in a fine state of division is obtained by the careful distillation of finely crystallised copper acetate. This is mixed with potassium nitrate, in the proportion of rather more than two equivalents of the former to one of the latter, and a little hot water. The mass is heated with constant stirring until dry, and then the temperature is raised cautiously, until ignition takes place. The mass is cooled, lixiviated, filtered quickly, and allowed to crystallise. Excess of copper removes every trace of nitrate. The copper oxide produced is very suitable for use in organic combustion. If the copper employed be less finely divided, the temperature required to bring about ignition is so high that more caustic potash than potassium nitrite is produced. J. T.

Affinity of Sodium Hydrate and Calcium Chloride for Water. By W. MÜLLER-ERZBACH (*Deut. Chem. Ges. Ber.*, xi, 409).—The author finds that solid sodium hydrate absorbs moisture from calcium chloride containing water of crystallisation. This is what might be expected from the fact that the contraction which takes place when sodium hydrate is dissolved in water, is greater than that which attends the solution of calcium chloride. W. C. W.

Calcium, Strontium, and Barium Oxides in the Crystalline State. By G. BRÜGELMANN (*Ann. Phys. Chem.* [2], ii, 466—475).—The paper describes in detail the mode of heating calcium, strontium, and barium nitrates in a porcelain flask, so that minute crystals of the corresponding oxides are obtained. These crystals belong to the regular system. The crystals of lime thus obtained can easily be seen to be cubes, and are found to take up moisture and carbonic acid much less readily than the amorphous quicklime obtained by heating marble. R. R.

Peculiar Oxidation of Aluminium. By A. HENZE (*Dingl. polyt. J.*, ccxxvii, 277—278).—Dr. C. Jehn and the author published a paper in the *Deut. Chem. Ges. Ber.*, 1874, p. 1498, on the oxidation of aluminium when rubbed with mercury or its salts. Further experiments have led to the following results.

The aluminium and mercury form a galvanic element which decomposes the moisture condensed upon them, the oxygen of which combines with the aluminium. With dry elements in a dry atmosphere there is no oxidation. Other electro-negative elements yield similar results. Aluminium pressed against moistened platinum becomes covered with alumina. The experiment succeeds also with silver, tin, and apparently also with gas coke; the latter gives a grey coating of alumina containing particles of aluminium. As in the case of the mercury experiment, the alumina increases in amount after being rubbed; this may be due to the gas which was polarised during contact subsequently acting on the metal. J. T.

Researches on Gallium. By A. DUPRÉ (*Compt. rend.*, lxxxvi, 720—722).—The sesquioxide obtained by heating the pure crystalline nitrate of the metal in a current of dry air at 200°, is decomposed when heated to redness in a current of hydrogen, with formation of a lower oxide of gallium soluble in dilute acids; this the author is investigating. C. F. C.

Carburation of Nickel by Cementation. By BOUSSINGAULT (*Compt. rend.*, lxxxvi, 509—513).—The author has made experiments with the view of ascertaining whether nickel would acquire the same properties as iron by carburation and tempering; if such were the case it might prove of much use, as by its addition to steel it might diminish oxidation. He first tried whether nickel, like iron, took up carbon by cementation; a plate of nickel, such as is used for nickel plating, was exposed in one of the cementation furnaces from April 25th till March 17th; when put in it contained no carbon, but small quantities of iron, arsenic, and copper; when taken out it was perfectly clean, showing no blisters, and possessing the same hardness as before. The plate weighed before cementation 1384 grams; after, 1389·25, having gained 5·25, and contained ·004 of combined carbon, without a trace of graphite. The plate was again cemented in a special box of sheet iron, filled with carbon; owing to an accident the box fused, and the nickel stuck to one of the bars of blister steel; it was therefore impossible to estimate directly the weight gained; but the analysis showed that the nickel now contained ·006 of carbon, about the same as that in soft steel. By fusing this metal in a crucible lined with charcoal, a button was obtained, containing ·0080 of combined carbon, and ·0165 graphite; total carbon, ·0245. Notwithstanding this high carburation, corresponding to hard steel, the nickel had the same appearance and ductility as before fusion. It is remarkable that the whole carbon taken up by the metal in this last operation was in the state of graphite. A small bar of forged nickel was also cemented, when it contained 98·29 p. c. of nickel, and 0·85 of combined carbon, besides small quantities of iron and silicon. The bar was placed in a clay crucible, surrounded with carbon, and exposed in the hottest part of a cementation furnace for a month; before cementation it weighed

201·907 grams, afterwards, 201·857; it therefore lost ·050 grams, but notwithstanding this, ·504 grams combined carbon, and ·303 graphite were taken up.

The carbon is the same as that found in tool steel; the bar showed no sign of any blister; it had kept its colour, density, ductility, and softness. From these experiments it would appear that although nickel combines with carbon, it does not acquire steel-like properties by so doing; the question whether carburised nickel retains magnetism better than the pure metal is now being studied by H. Becquerel. The author concludes the paper by discussing the question whether or not an addition of nickel preserves iron and steel from rust; to obtain this result a large percentage of nickel must be used.

J. M. T.

Presence of Lead in Nitrate of Bismuth. By A. CARNOT (*Compt. rend.*, lxxxvi, 718—720).—The author has analysed several preparations of the bismuth nitrate employed in pharmacy, in which the presence of lead had been detected. Operating upon ten grams of the nitrate, he obtained from seven different samples the following quantities of lead respectively:—0·011, 0·016, 0·023, 0·032, 0·038, 0·065, 0·098 gram. These results should serve as a caution to those engaged in preparing and dispensing this drug.

The analytical method employed by the author is given in detail.

C. F. C.

Action of Various Fatty Oils on Copper. By W. H. WATSON (*Chem. News*, xxxvi, 200).—8 square inches of copper surface were exposed to 500 water-grain measures of oil:—

Oil.	Grains of copper in solution after 10 days.	after 77 days.
Linseed	0·3	0·5435
Olive	0·22	0·24
Colza	0·017	0·14
Almond	0·103	0·22
Seal	0·0485	0·08
Sperm	0·003	0·06
Castor	0·0065	0·01
English neatsfoot	0·11	—
Sesame	0·17	—
Paraffin	0·0015	0·003

M. M. P. M.

A New Product of the Oxidation of Lead, and some Phenomena of Dissociation. By H. DEBRAY (*Compt. rend.*, lxxxvi, 513—517).—Two methods of preparing minium are known, the one by oxidation of yellow lead protoxide, at a temperature of about 500°, the other by heating lead binoxide at 440° under atmospheric pressure. It is evident that the yellow protoxide can give no higher oxide than minium, as any such oxide would not be stable at the temperature of formation of the latter. If, however, the binoxide be heated at 350° only, the decomposition, which at first is very rapid, gradually becomes slower, and if the operation be stopped when the decomposition has nearly ceased, it will be found that the binoxide has been converted into a neutral plumbate of the protoxide ($PbO.PbO_2$) having a greenish-brown colour, and intermediate in composition and reactions between minium and the binoxide. This plumbate is also formed when oxygen or air is passed over protoxide or carbonate of lead at 350°. The author points out that the conversion of protoxide into sesquioxide is never complete at 350°, but, on the contrary, if the oxidation be continued long enough (seven to eight days) it becomes wholly reconverted into minium: this phenomenon being analogous to the conversion of sesquioxide of iron into magnetic oxide at a high temperature, when the latter is found to be incapable of reproducing sesquioxide.

From his results the author considers that it cannot be said that any compound directly formed will of necessity undergo a limited decomposition at a certain temperature; for such to be the case it is necessary that the elements of the body separated by heat should be capable of recombining. In reacting on each other, the greater number of compounds satisfy this condition, but the influence of heat may, under certain circumstances, so modify the state of the substance as to render it incapable of entering into combinations which it might be able to form when it is itself obtained under different conditions. J. M. T.

Amalgamation of Iron and some other Metals. By CASAMAJOR (*Arch. Pharm.* [3], xi, p. 464).—Iron, platinum, palladium, aluminium, nickel, and cobalt, can be easily amalgamated by placing them in contact with mercury and a zinc rod, and covering with acidulated water. The amalgamated iron is completely permeated by the mercury, although the amount of the latter metal present is exceedingly small. The amalgamated aluminium when dry becomes very hot, the mercury appears to boil, and the surface is rapidly covered with a chalky incrustation. E. N.

Crystalline Form and Optical Properties of Mercurous Iodide. By A. DESCLOIZEAUX (*Compt. rend.*, lxxxiv, 1418—1421).—The crystallographic measures of mercurous iodide, Hg_2I_2, are almost identical with those of mercurous chloride, Hg_2Cl_2, and the crystals of both substances have a powerful double refraction with positive axis. The crystals of mercurous iodide are also nearly geometrically isomorphous with those of mercuric iodide, HgI_2, but optically their double refraction has the opposite sign, its axis being negative.

Berthelot considers these facts to show that the inferences from the isomorphism of compounds, as to their containing the same number of atoms, or having isomorphous constituent elements, cannot be relied on. R. R.

Mineralogical Chemistry.

On Native Iron. By De Chancourtois (*Jahrb. f. Min.*, 1877, 837).—The author after treating of the importance of cyanogen in the production of metallic iron, both in the blast furnace and in nature, calls attention to the iron mass lately found at St. Catharina, which contains 36 per cent. of nickel, and, like the iron of Ovifak, is of terrestrial origin. G. T. A.

Some Minerals formed by the Volcanic Vapours of Vesuvius. By G. v. Rath (*Jahrb. f. Min.*, 1877, 826—827). After the eruption of April 26th, 1872, numerous minerals were found amongst the sublimation products, including various silicates and fine crystals of apatite, together with iron pyrites in several forms, and large quantities of tenorite. The crystals of the latter mineral without losing their shape, have been altered by the hydrochloric acid escaping from the fumeroles, into a green body, which contains 45·59 of cupric oxide, 38·19 of cuprous chloride, and 16·22 of water; the name of ateline has been given to it. Sylvine and sodium chloride were found in large quantities, and generally mixed together. Sal-ammoniac was abundant and in the finest crystalline forms, but not in octahedrons; it was also found in the fumeroles in beautiful yellow crystals, formed after the colourless ones. The crystals were black at a spot where a charred tree stump lies buried in the lava. Fluorine was found in combination with ammonia and silica, probably as a double salt, $2NH_4F.SiF_4$, for which the name *cryptohalite* has been proposed. Calcium chloride occurred in large quantities; it seems to have been formed at the beginning of the eruption; cotunnite was abundant. A new mineral, *erythrosiderite*, consists of red rhombic crystals. Iron chloride ($Fe_2Cl_6 + xH_2O$) occurs in the clefts of the lava, and is often mistaken for sulphur. Sodium-potassium sulphate, aphthalos, or aphthithalite, was found in white hexagonal laminæ. Anhydrite was not so common. Hydrofluoric acid was found inside the crater in masses of gypsum and sulphur. G. T. A.

Some American Pyrrhotites and other Minerals containing Nickel. By H. How (*Jahrb. f. Min.*, 1877, 834).—Pyrrhotite often contains nickel as well as cobalt. The author finds that the intensity of the magnetic properties of the mineral varies greatly, and that it is feeblest when the largest quantity of nickel is present. Specimens from the same locality may contain very different amounts of nickel. Mispickel from Montague, Halifax Co., Nova Scotia, contained 0·09 per cent. of cobalt; mispickel containing nickel and cobalt is found in Lüneburg Co. in crystals of rare beauty. G. T. A.

Zinc Ores from the New Helene Mine at Scharley, near Beuthen, Silesia. By A. Lindner (*Deut. Chem. Ges. Ber.*, xi, 394—398).—This mine is chiefly worked for red and white calamine, which are found associated with zinc blende, zinc silicate, and galena, between layers of dolomite and marl. Pure crystalline zinc spar, blende, and silicate, are of rare occurrence.

The composition of the red calamine is shown by the following analyses:—

	$CaCO_3$.	$MgCO_3$.	$ZnCO_3$.	$Zn_2SiO_4.H_2O$.	$2Fe_2O_33H_2O$.	Moisture.	
1.	9·44	8·21	45·39	16·22	14·12	6·43	= 99·81
2.	16·38	9·12	36·12	23·05	14·50	0·54	= 99·71
3.	37·02	20·56	17·00	7·29	18·07	0·00	= 99·94

The amount of zinc and sulphur in different samples of blendes varies from 64 to 39·4 per cent. Zn, and from 27·94 to 1·58 per cent. S.

The following analyses show the composition of (1) black blende and (2) white blende.

	H_2O.	Fe_2O_3.	Zn.	S.	CaO.	MgO.	CO_2.	Pb.	
1.	1·56	1·00	47·47	25·07	3·68	2·51	5·65	12·22	= 99·16
2.	0·90	1·44	61·94	30·27	1·27	0·89	2·43	0·0	= 99·14

W. C. W.

Artificial Formation of Brochantite. By S. MEUNIER (*Compt. rend.*, lxxxvi, 686).—This has been effected by the author by allowing fragments of galena to remain for a period of eleven months in a solution of copper sulphate. The brochantite was deposited in the form of radiating crystalline masses, of an emerald-green colour, upon the surface of the corroded sulphide. Lead sulphate was also formed in considerable quantity. Since this mineral has been found by M. Delafosse to occur in Hungary in association with galena, and also by Magnus to contain lead, the author's results in all probability indicate its natural origin. C. F. C.

The Deposits of Calcium Phosphate in Estremadura. By A. DELESSE (*Jahrb. f. Min.*, 1877, 834).—The phosphate occurs sometimes as apatite in bright green crystals, sp. gr. 3·04—3·41; at others as phosphorite in coarse-grained masses, sp. gr. 2·6—3. Apatite contains 90 to 100 per cent. of calcium phosphate, and is always accompanied by quartz. Phosphorite is generally intermixed with gangue, and contains 75—85 to 100 per cent. of phosphate. Fluorine and chlorine are always present in the calcium phosphate of Estremadura. The calcium phosphate forms vein-like layers in the granite, in the palæozoic slates, and Devonian limestones. The vein in the slates of Costanaza at Logrosan has been followed for six kilometres; its mean breadth is about three meters. The mineral has probably been deposited in the fissures by mineral springs.

G. T. A.

Nepheline, Monacite, and Silver Bismuth-glance. By C. RAMMELSBERG (*Jahrb. f. Min.*, 1877, 830—831).—I. Nepheline from Vesuvius, sp. gr. 2·600—2·6087. Analysis indicates that this mineral is a combination of mono- and bisilicates, $5Na_2AlSi_2O_8 + K_2AlSi_4O_{12}$. II. Monacite from Arendal, sp. gr. 5·174. The simple formula for this specimen is $RP_2O_8 = (Ce,La,Di)_2P_2O_8$. III. Silver bismuth-glance from Matilda Mine, Morococha, Peru, is found mixed with fahl-ore, lead glance, and blende, sp. gr. 6·92; consists of $Ag_2S + Bi_2S_3 = AgBiS_2$. G. T. A.

A New Locality for Alunite. By H. CREDNER (*Jahrb. f. Min.*, 1877, 833).—Concretions of alunite in great abundance occur in the white quartz sand overlaid by peat at an opening in the western slope of the Muldenthal above Harkort's factory, near Wurzen. This mineral has hitherto been found only among volcanic rocks. G. T. A.

The Pyrogenic Quartz in the Lavas of the Lower Rhine. By J. LEHMANN (*Jahrb. f. Min.*, 1877, 847).—The author thinks that the specimens of quartz, &c., are formed by crystallisation from molten masses formed by the fusion of rocks included in the lava. The crystals of quartz usually exhibit the combination $\pm R. \pm \frac{3}{2}R. \infty R$. Accompanying them are augite, felspar, and tridymite. The occurrence of the two modifications of silicic acid in combination is worthy of note; it shows how slight the modification of conditions need be to produce the same chemical compound in the one or the other form.

G. T. A.

A Contribution to our Knowledge of Palæopicrite and its Products of Decomposition. By K. OEBBEKE (*Jahrb. f. Min.*, 1877, 844—846).—After general remarks on olivine rocks and their distribution (together with the literature of the subject), the author treats of two olivines from the neighbourhood of Dillenburg, Nassau.

The Black Stones of Wallenfels form a ridge of which the highest point is 513·85 meters above the sea level. The olivine rock is a palæopicrite of a very dark green colour. It contains the following minerals: a bright green olivine, which the author calls lime-olivine, a brown mica, leek-green chrome-diopside, plates of hypersthene, deep black specks of picotite, and particles of magnetic iron ore. In the clefts of the rock, and combined with it in all possible transitions, is a bright-green serpentine. Microscopic investigation showed the mesh-structure characteristic of olivine rocks in conversion into serpentine, and also a dark green colour of the ground-mass, probably due to nickel. White particles of magnesite were sprinkled here and there.

The following analyses were made:—

I. Black stones. II. "Hülfe Gottes" Mine.

	SiO_2.	MgO.	CaO.	NiO.	MnO.	FeO.
I.	39·103	29·176	3·951	0·162	0·276	11·441
II.	41·311	21·380	3·279	0·666	0·378	7·339

	Fe_2O_3.	Al_2O_3.	Cr_2O_3.	H_2O.
I.	4·315	4·940	0·446	5·669
II.	13·892	2·432	1·251	7·124

Traces of copper, bismuth, cobalt, sulphur, phosphoric acid, carbonic acid, potassium. No. II also contained 0·776 of iron sulphide.

The green decomposition-product consists of—

SiO_2.	MgO.	CaO.	FeO.	Fe_2O_3.	Al_2O_3.	H_2O.
42·878	32·220	0·095	4·821	3·866	1·832	14·214

Sp. gr. 2·51. It is therefore a serpentine rich in iron, closely allied to baltimorite.

The chrome-diopside (sp. gr. 3·202) contains—

SiO_2.	MgO.	FeO.	Cr_2O_3.	Al_2O_3.	CaO.
50·443	17·418	9·696	1·403	5·105	14·629

The olivine—

SiO_2.	MgO.	CaO.	MnO.
42·531	35·682	14·088	6·483

may be called a lime-olivine, as half the magnesia has been replaced by lime.

The rocks at the old nickel mine of "Hülfe Gottes" at Nanzenbach consist of a similar palæopicrite, as is shown by the analysis given above.

The petrographical, microscopical, and chemical characters of the two series show that both are undergoing conversion into serpentine, but that the decomposition has reached a more advanced stage at the latter locality. The olivine, from which the serpentine is chiefly formed, stands midway between typical olivine and monticellite, on account of the amount of lime which it contains. This large amount of lime seems to be characteristic of the olivines of the eruptive rocks of the picrite-group. The author also gives details of his chemical methods, plates of sections, &c. G. T. A.

Investigation of two Magnesia Micas. By F. BERWERTH (*Jahrb. f. Min.*, 1877, 830).—I. Phlogopite, containing barium from Edwards, St. Lawrence Co., N.Y., occurs in brown transparent folia. Sp. gr. 2·959. II. Mica from Vesuvius. Hexagonal leek-green plates, often in combination with vesuvian. Sp. gr. 2·864.

Analyses :—

	F.	SiO_2.	Al_2O_3.	Fe_2O_3.	BaO.	MnO.	FeO.
I.	0·82	40·34	15·14	2·20	2·46	—	0·77
II.	0·89	39·30	16·95	0·48	—	0·59	7·86

	MgO.	CaO.	K_2O.	Na_2O.	H_2O.
I.	27·97	—	7·07	2·58	3·21
II.	21·89	0·82	7·79	0·49	4·02

G. T. A.

Chabasite. By A. STRENG (*Jahrb. f. Min.*, 1877, 725—728).—The following numbers give the mean of a series of analyses of chabasites :—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	K_2O.	Na_2O.	H_2O.
I.	46·35	20·52	—	10·83	0·21	—	22·09
II.	50·75	16·06	1·43	6·65	2·27	1·38	21·46
III.	48·93	18·19	1·22	6·64	2·06	0·92	22·04
IV.	46·82	19·29	0·14	10·29	0·40	0·70	22·36

I is from Nidda; II, from Altenbuseck; III and IV, from Annerod.

The crystalline form of I, II, III consists only of the fundamental rhombohedron. Intersection twins are everywhere present, and sometimes also contact twins. The phacolite No. IV exhibits the forms $\frac{2}{3}P2.—2R.—\frac{1}{2}R + R$, and occurs only in intersection twins (0R).

Pseudomorphs of mesotype or skolezite after phacolite are found here and there.

The proportion Al : Si is in the chabasite from Nidda 1 : 3·85, in the phacolite from Annerod 1 : 4·12, in chabasite from Annerod 1 : 4·4, in chabasite from Altenbuseck 1 : 5·09.

The union of levyn, gmelinite and phacolite with chabasite is prevented only by their difference in cleavage.

Some optical irregularities of chabasite are accounted for by the disturbances of the planes of the forces forming the crystal, caused by the presence of a second crystal, which penetrates the first, and is in such a position with respect to it that the edges and angles of the one take the place of the planes of the other. The molecules are thus out of their natural position, and tensions are produced which may cause a uniaxial crystal to appear biaxial.

An extensive series of angular measurements of chabasites from various localities shows that the angle between the terminal edges is only 94° 46′ when the two planes which enclose it are not disturbed by a twin crystal. This is seldom the case, so that the angle varies between 94° 35′ and 99° 7′.

Tables of analyses of chabasites, phacolites, levyns, and gmelinites are referred to in the paper, from which it is seen that the proportion of Al : CaK_2Na_2 in the majority of cases is 1 : 1; that of Al : Si, however, varies between 1 : 3·13 and 1 : 5·52. The quantity of water also varies, so that the atomic proportion of Al : H ranges from 1 : 9·62 to 1 : 15·2. As a rule the quantity of H increases with that of Si. Hence the above named minerals form a series which, starting from $(CaK_2Na_2)AlSi_3O_{10} + 5H_2O$, gradually passes into—

$$(CaK_2Na_2)AlSi_5O_{14} + 3H_2O.$$

This may be accounted for in two ways: either the chabasites and the allied minerals are isomorphous mixtures of two hypothetical and isomorphous terminal members—

$$\text{(1.) } H_8RAlSi_2O_{12} = H_{16}RAlRAlSi_4O_{24},$$
$$\text{(2.) } H_{16}RAlSi_6O_{24} = H_{16}RAlSi_2Si_4O_{24},$$

or they consist of $AlSi_3O_9FCaSiO_3$ + varying quantities of the bisilicate, H_2SiO_3.

Determinations of specific gravity of various chabasites showed that in general the specific gravity decreases in proportion as the quantity of Si increases. G. T. A.

Garnierite. By J. GARNIER (*Compt. rend.*, lxxxvi, 684—686).—The author substitutes, on the results of numerous analyses, the formula $(\dot{M}g\dot{N}i)\ddot{S}i + 4\dot{H}$, for that given by Dana, viz., $(\dot{M}g\dot{N}i)_{10}\ddot{S}_{18} + 3\dot{H}$, for this mineral.

The following analysis is given of a garnierite, which formed a thin coating of a bright green colour over a magnesium gangue:—

SiO_2.	NiO.	FeO.	Al_2O_3.	CaO.	MgO.	H_2O.
44·40	38·61	0·43	1·68	1·07	3·45	10·34.

The ratio of the oxygen in the silica to that in the bases being as 2 : 1.

The various forms of garnierite all exhibit freedom from arsenic and sulphur, and cannot therefore be products of decomposition of sulphides or arsenio-sulphides. C. F. C.

A Variety of Cronstedite. By F. FIELD (*Phil. Mag.* [5], v, 52—54).—The author has examined an amorphous, dark leek-green mineral, occasionally found associated with cronstedite, in Cornwall. Its specific gravity was 3; hardness, about 2·5. On heating, water was evolved, and the green powder rapidly passed into yellowish-brown. An analysis showed ferrous oxide, 39·46; ferric oxide, 18·51; silicic acid, 31·72; water, 11·02 per cent. It is remarkable that the proportions of water and ferrous oxide are much the same as in cronstedite, whilst silicic acid and ferric oxide appear to have changed places, Maskelyne and Flight having found in cronstedite, silicic acid 18·54 and ferric oxide 32·75 per cent. R. R.

A New Copper Ore and its Metallurgy. By S. HUNT (*Jahrb. f. Min.*, 1877, 837).—An earthy green copper ore is found at Jones Mine, Springfield, Berks Co., Pennsylvania, together with magnetic iron ore and copper pyrites, which contains—

SiO_2.	Al_2O_3.	MgO.	Fe_2O_3.	CuO.	H_2O.	Insol. sand.
24·60	13·00	15·15	7·11	15·30	11·50	14·10

and for which the name of *venerite* is proposed. It is infusible, soluble in hot concentrated sulphuric acid, and requires for reduction a previous treatment at a red heat with bodies yielding carbonic acid. G. T. A.

The Eruptive Formation of Fleims, with some Remarks on Formations of the Older Volcanoes. By C. DOELTER (*Jahrb. f. Min.*, 1877, 846).—A comparison of the eruptive formations of the South Tyrol with tertiary volcanoes. The eruptive rocks of Fleims afford a peculiar instance of volcanic masses, in which the characters of the older eruptive rocks are mixed with those of the tertiary period. G. T. A.

Analysis of the Water of the Danube at Buda-Pesth. By BALLO (*Deut. Chem. Ges. Ber.*, xi, 441—445).

	Gram per litre.
Total suspended matter (mean of 13 monthly determinations	0·1435
Total matter in solution (mean of 9 monthly determinations)	0·1869

Mineral Constituents of 1 *Litre Water* (*November*, 1872).

Acid calcium carbonate	0·1227
,, magnesium carbonate	0·0633
Calcium sulphate	0·0292
Sodium chloride	0·0035
Iron oxide	traces
Silica	0·0018
Carbonic acid	0·0163
Total matter in solution	0·2368
,, ,, suspension	0·1792

Composition of Suspended Matter (*Average for March*, 1872).

	In HCl.	
	Soluble.	Insoluble.
Silica	—	45·95
Al_2O_3	8·62	9·28
FeO	2·59	—
Fe_2O_3	1·38	—
CaO	5·53	0·46
MgO	0·30	2·44
K_2O	0·52	1·90
Na_2O	0·26	5·22
CO_2	5·35	—
H_2O	3·86	—
Organic matter	—	6·65
	28·41	71·90

C. F. C.

Organic Chemistry.

Nature of the Hydrocarbons produced by the Action of Acids on White Specular Manganiferous Cast-Iron. By S. Cloez (*Compt. rend.*, lxxxv, 1003).—A white cast-iron, containing 0·04 per cent. of combined carbon, and 0·06 per cent. of manganese, when treated with hydrochloric acid of sp. gr. 1·12, or better, with sulphuric acid, diluted with 6 parts of water, gave liquid and gaseous hydrocarbons homologous with ethylene, which were absorbed by bromine, and combined easily with hydrochloric acid; besides these, methane-derivatives, insoluble in sulphuric acid, were produced.

200 kilos. of cast-iron, treated with sulphuric acid, gave (1) 640 grams of oily hydrocarbons condensed in the first wash-bottles; (2) 2780 grams of brominated ethylenic compounds; (3) 532 grams of hydrocarbons homologous with methane (paraffins), isolated by sulphuric acid; (4) 3800 grams of insoluble residue; and (5) 408 grams of an oily body, extracted from the insoluble residue by alcohol, and separated from the alcohol by water.

The paraffins, decanted from the sulphuric acid, washed with water, and dried, first with potassium hydrate, and then with sodium, were fractionally distilled; the liquid began to boil at 155°, and the thermometer rose gradually to 300°.

The following table gives the compounds isolated:—

Name of Compound.	Formula.	Boiling point.	Sp. gr.
Decane	$C_{10}H_{22}$	155—160°	0·760
Undecane	$C_{11}H_{24}$	178—180°	0·769
Dodecane	$C_{12}H_{26}$	195—198°	0·782
Tridecane	$C_{13}H_{28}$	215—220°	0·793
Tetradecane	$C_{14}H_{30}$	234—238°	0·812
Pentadecane	$C_{15}H_{32}$	358°	0·830
Hexdecane	$C_{16}H_{34}$	276—280°	0·850

The vapour-densities of the first two are 5·132 and 5·521 respectively. The compounds are all colourless, mobile liquids, attacked by chlorine and bromine, but not acted on by sulphuric acid. Hexdecane is attacked by fuming nitric acid. C. W. W.

Synthesis of Olefines. By A. ELTEKOFF (*Deut. Chem. Ges. Ber.*, xi, 412—414).—By heating a mixture of amylene and methyl iodide with excess of dry lead oxide at 210° for several hours, a product boiling between 36° and 85° is obtained, one-third of which comes over between 70° and 83°, and consists of a mixture of C_6H_{12} and C_7H_{14}; this portion forms with bromine a solid compound, apparently $C_6H_{12}Br_2$, melting at 139—140°. The hydrocarbons dissolve in sulphuric acid (2 acid to 1 OH_2), and on the addition of water a liquid and a solid body separate out. The latter, which is the hydrate $2(C_7H_{16}O) + H_2O$ of Butlerow's *pentamethylethol*, melts at 75°. The action of fuming hydrochloric acid on the mixed olefines also gives rise to a solid product, melting at 100°, and boiling at 120—125°, which appears to be a mixture of $C_6H_{13}Cl$ and $C_7H_{15}Cl$.

The author has also found that olefines are formed by the action of lead oxide on alcoholic chlorides, bromides, and iodides, at 220°. Isobutyl iodide is thus completely decomposed, $2C_4H_9I + PbO = C_4H_8 + PbI_2 + H_2O$, and isoamyl iodide gives an amylene isomeric with that obtained by the action of alcoholic potash. W. C. W.

Action of Boron Fluoride on Carbon Compounds. By F. LANDOLPH (*Compt. rend.*, lxxxvi, 671—673).—*Benzoic aldehyde*, at its boiling point, unites directly with an equivalent of BF_3, the resulting compound crystallising in brilliant plates (hexagonal). Heated at 250° in sealed tubes, it yields a black mass, containing about 20 per cent. of benzoic acid, and a gaseous mixture of BF_3, CO, CO_2, and C_2H_2.

Ethylene and boron fluoride react, under the combined influence of light and heat (30°), according to the equation:—

$$C_2H_4 + BF_3 = C_2H_3.BF_2 + HF.$$

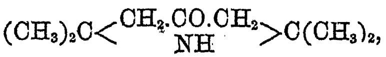
The product, $C_2H_3.BF_2$, is an ethereal liquid, boiling at 124—125°, and of specific gravity, 1·0478 at 23°; it volatilises in the air with formation of white fumes. Its composition has been established both by analysis and by the determination of its vapour-density. Its decomposition by water may be represented thus:—

$$C_2H_3.BF_2 + 3H_2O = B(OH)_3 + C_2H_4 + 2HF.$$

C. F. C.

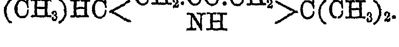
Cause of the Formation of Vinyl-diacetonamine. By W. HEINTZ (*Liebig's Annalen*, cxci, 122—125).—In a former publication (*Annalen*, clxxxix, 214) the author expressed the opinion that the formation of vinyl-diacetonamine from acetone was due to some impurity in the acetone. Further investigation has shown this to be correct, and that the presence of aldehyde is necessary, for when the acid oxalate of diacetonamine is boiled with alcohol and aldehyde for some time, vinyl-diacetonamine oxalate is produced, agreeing in all its properties with that previously described by the author (*loc. cit.*).

The author considers the relationship of triacetonamine to vinyl-diacetonamine to be similar to that existing between aldehyde and acetone, the latter being the first homologue of the former. Triacetonamine, which is formed by the action of acetone on diacetonamine, differs from vinyl-diacetonamine, inasmuch as it contains three acetone residues, whilst the latter contains two acetone and one aldehyde residue. If the structural formula for triacetonamine be—



$$(CH_3)_2C<\substack{CH_2.CO.CH_2\\NH}>C(CH_3)_2,$$

then that of vinyl-diacetonamine is most probably



$$(CH_3)HC<\substack{CH_2.CO.CH_2\\NH}>C(CH_3)_2.$$

P. P. B.

Action of Zinc-ethyl and Zinc-methyl on Bromacetyl Bromide. By W. WINOGRADOW (*Liebig's Annalen*, cxci, 125—142).—The author gives a short historical sketch of this and similar investigations which have been carried on in Butlerow's laboratory, and have led to unsatisfactory results, owing, as the author demonstrates, to the proportion of zinc-compounds used being insufficient.

Bromacetyl Bromide and Zinc-methyl.—In this reaction the quantities taken were 1 molecule of bromacetyl-bromide to 3 molecules of zinc-methyl, the former being added in small quantities to the latter, and kept well cooled to moderate the violence of the reaction. The product, a yellowish-brown viscous liquid, began to deposit crystals in the course of two or three days, apparently consisting of $ZnCH_3Br$ and $ZnBr_2$. After the lapse of 20—30 days, the product was decomposed with snow and water, when a combustible gas was evolved, and zinc oxide separated out. This was dissolved in hydrochloric acid, and the alcohol formed was distilled off from the zinc chloride. The distillate, after drying over potassium carbonate, was fractioned, and the larger portion, coming over between 110—120°, was dried over anhydrous baryta, and treated with sodium at the boiling point to remove all bromine. The alcohol thus obtained boils at 113°, has a peculiar feeble odour, is easily soluble in water, and does not solidify at $-33°$. Analysis shows its formula to be $C_5H_{12}O$; its specific gravity at 0° is 0·8308; at 19°, it is 0·8219; therefore, its coefficient of expansion for 1° between 0° and 19° is 0·00156. Bromine acts on it as it does on many secondary and tertiary alcohols, forming an amylene, which further unites with bromine to form amylene bromide. PCl_5 acts on it, yielding a chloride $C_5H_{11}Cl$, which is a colourless liquid, boiling at 86—87°.

Gaseous hydriodic acid reacts on this alcohol to form an iodide, $C_5H_{11}I$, which, when freshly distilled, is almost colourless, but becomes brown on standing; the iodide boils at 127—129°, and has a specific gravity at 0° of 1·522, and at 18° of 1·498, thus having a coefficient of expansion of 0·000092 for 1° between 0° and 18°. In the preparation of the iodide, it was observed that hydriodic acid does not act on the alcohol in the cold, but the iodide is formed directly on gently heating. This behaviour with hydriodic acid is identical with that observed by Wischnegradsky in the case of the alcohol prepared from methylisopropyl ketone. The iodide so prepared is not a secondary, but a tertiary one, as shown by the boiling point, and by its no longer yielding the original methylisopropyl alcohol when treated with moist silver oxide, but an alcohol boiling at 102—104°, which is dimethylethyl carbinol. This alcohol is formed by the withdrawal of the elements of water from the secondary alcohol, and the subsequent addition of the elements of water to the olefine thus produced, as expressed in the following equations:—

$$(CH_3)_2CH.CH(CH_3)(OH)-H_2O = (CH_3)_2C{=}CH.CH_3,$$
$$(CH_3)_2C{=}CH.CH_3 + H_2O = (CH_3)_2C(OH).CH_2.CH_3.$$

The alcohol produced by action of zinc methyl on bromacetylbromide yields, on oxidation, methylisopropyl ketone, boiling at 93—94°, and forming with sodium hydrogen sulphite a crystalline compound. On further oxidation, acetone and acetic acid are produced, so that the original alcohol is methylisopropyl carbinol. Methylisopropyl ketone has a specific gravity at 0° of 0·8123, and at 19° of 0·8051; therefore, its coefficient of expansion for 1° between 0° and 19° is 0·00118.

Besides the methylisopropyl carbinol formed in the above reaction, it appears that the fraction distilling over below 100° contains acetone, and probably methylethyl ketone, whilst that which comes over at 125—180° consists of an oil containing over 30 per cent. Br, which is probably a brominated acetone, and a liquid whose properties resemble those of the condensation-product of methylethyl ketone, already described by Pawlow (*Jour. Russ. Chem. Soc.*, viii, 321).

Concerning the mechanism of the action of zinc-methyl on bromacetyl bromide, the author advances the following as probable explanations. The first product of the reaction is $CH_2Br.CBr(CH_3).OZnCH_3$, which, with water, would yield a brominated acetone. By the further action of zinc-methyl, the following products would be obtained:—

$$\begin{gathered} CH_2Br.CBr(CH_3).OZnCH_3 + Zn(CH_3)_2 = \\ CH_3.CH_2.CBr(CH_3).OZnCH_3 + Zn(CH_3)Br \end{gathered} \qquad (A),$$

$$\begin{gathered} CH_2Br.CBr(CH_3).OZnCH_3 + Zn(CH_3)_2 = \\ CH_3Zn.CH_2.CBr(CH_3).OZnCH_3 + CH_3Br \end{gathered} \qquad (B).$$

On decomposition with water, the product formed, according to (A), would yield methylethyl ketone, whilst that in B would give acetone.

The action by which methylisopropyl carbinol is formed is analogous to that of zinc-methyl on ethylene iodhydrin, by which a secondary alcohol is formed (Butlerow and Ossokin, *Annalen*, cxlv, 257). The first product of this reaction is $CH_2I.CH_2.OZnCH_3$, and this undergoes a molecular change, passing into the ethylidene series, $CH_3.CHI.OZnCH_3$, being formed. Now the compound,

$$CH_2Br.CBr(CH_3).OZnCH_3,$$

or still better, $CH_2Br.C(CH_3)_2.OZnCH_3$, may be viewed as analogous to $CH_2I.CH_2.OZnCH_3$, and the latter, undergoing molecular change, would yield $(CH_3)_2CH.CHBr.OZnCH_3$, which, when the bromine has been replaced by CH_3, yields with water methylisopropyl carbinol.

A second explanation is that the compound,

$$CH_2Br.CBr(CH_3).OZnCH_3,$$

decomposes under the influence of $Zn(CH_3)_2$ into HBr and $CHBr{=}C(CH_3).OZnCH_3$; the HBr reacts on $Zn(CH_3)_2$ to form $ZnCH_3Br$; and the methyl and H unite with the above group to form $(CH_3)CHBr.CH(CH_3).OZnCH_3$.

This compound, after replacement of Br by CH_3, would yield with water the secondary alcohol required.

Another explanation of the reaction may be offered. In the formation of amyl-hydroxalic acid by the action of amyl iodide and zinc on ethyloxalic ether (Frankland and Duppa, *Annalen*, clxii, 5), the amyl and zinc-mono-amyl take the place of O, and in like manner, in the action of zinc-methyl and bromacetyl-bromide, the methyl and zinc-monomethyl groups may be supposed to take the places of the bromine and hydrogen, thus giving rise to the compound, $CH_3.CHBr.C(CH_3)(ZnCH_3).OZnCH_3$, which, when the Br is replaced by CH_3, would yield, on decomposition with water, the secondary alcohol.

Lastly, as suggested to the author by M. Kaschirsky, it may be supposed that the compound, $CH_2Br.C(CH_3)_2.OZnCH_3$, is first formed, and decomposes as follows:—

$$CH_2Br.C(CH_3)_2.OZnCH_3 = CH_2.O.C(CH_3)_2 + ZnCH_3Br.$$

The oxide thus formed changes into an aldehyde, which, under the influence of zinc-methyl, forms the secondary alcohol, methylisopropyl carbinol.

By the action of zinc-ethyl on bromacetyl bromide and decomposition of the product with water, an octyl-alcohol is formed, which is slightly soluble in water, and boils at 164—166°. It does not solidify at −30°. Treated with PCl_5, it yields a chloride; and an iodide by action of gaseous hydriodic acid. Supposing the action of zinc-ethyl to be analogous to that of zinc-methyl on bromacetyl bromide, this octyl alcohol probably has the constitution, $CH(C_2H_5)_2.CH(OH).C_2H_5$.

P. P. B.

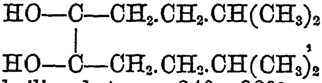
Ethylic Isobutylacetoacetate, Methylisamyl Carbinol, and Isobutylacetic Acid. By W. ROHN (*Liebig's Annalen*, cxc, 305—322).—*Ethylic Isobutylacetoacetate*,

$$CH_3.CO.CH.CH_2.CH(CH_3)_2.COOC_2H_5,$$

was prepared by the action of isobutyl iodide on sodacetoacetic ether, obtained by treating a mixture of equal volumes of acetoacetic ether and benzene with sodium. It is a colourless oil, with a feeble odour, boiling at 217—218°, and having a sp. gr. of 0·951 at 17·5°. On being boiled with baryta water, it split up into isamylmethyl ketone, with some barium isobutylacetate.

Isamylmethyl ketone, $CH_3.CO.CH_2.CH_2.CH(CH_3)_2$, is a colourless, limpid liquid, not miscible with water, and having a powerful odour resembling that of amyl acetate. It boils at 142—144° (uncor.), and has a sp. gr. of 0·8175 at 17·2°. With sodium bisulphite, it yields a mass of white pearly crystals. On being dissolved in ether floating on a layer of water, and reduced by nascent hydrogen generated by the addition of sodium, it yields a mixture of di-isobutylpinacone and methylisamyl carbinol.

Di-isobutyl pinacone,



$$\begin{array}{l}\mathrm{HO{-}C{-}CH_2.CH_2.CH(CH_3)_2}\\ \quad\;| \\ \mathrm{HO{-}C{-}CH_2.CH_2.CH(CH_3)_2}\end{array}$$

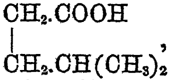
, is an oily liquid, insoluble in water, and boiling between 240—260°.

Methylisamyl carbinol,

$$C_7H_{15}HO = CH(OH)(CH_3).CH_2.CH_2.CH(CH_3)_2,$$

is a colourless limpid liquid, boiling at 148—150°, not solidifying at −16°, and having a sp. gr. of 0·8185 at 17·5°. The *acetate* is an oily liquid, which boils at 166—168°. The *chloride*, $C_7H_{15}Cl$, forms a colourless oil, having a peculiar odour, and boiling between 135—137°. The *iodide* boils at 175°.

Isobutylacetic acid,



$$\begin{array}{l}\mathrm{CH_2.COOH}\\ |\\ \mathrm{CH_2.CH(CH_3)_2}\end{array}$$

, obtained together with isamylene-ethyl ketone and acetic acid by saponification of ethylic isobutylacetoacetate, is a colourless oilyl iquid, with an odour like that of caproic acid, and boiling at 198·6—199·8°. The *silver* salt forms minute anhydrous crystals. The *barium* salt forms pearly anhydrous needles, of which water dissolves 19·95 per cent. at 14°, and 20·3 per cent. at 19°. The *calcium* salt is also anhydrous, and water dissolves 9·0 per cent. at 19°.

E. N.

Action of Potassium Cyanide and of Alcoholic Potash on Acetyl Chloralacoholate and Tetrachlorether. By J. BUSCH (*Deut. Chem. Ges. Ber.*, xi, 445—447).—The action of alcoholic potash upon Henry's tetrachlorether, $CCl_3.CHCl.OC_2H_5$, gives rise to an unsaturated ether of the formula, $CCl_2{=}CCl.OC_2H_5$, a heavy colourless oil, boiling at 155°. The unsaturated condition of this ether is evinced by the ease with which it combines with chlorine, forming the compound, $C_2Cl_5.OC_2H_5$, a colourless liquid which fumes in the air, and boils with partial decomposition at about 200°, whilst with bromine it yields $CCl_2Br.CClBr.OC_2H_5$, a colourless oil, which forms large transparent crystals, melting at 17°. By the action of silver acetate (alcoh. sol.) upon the latter, one atom of bromine and one of chlorine appear to be replaced by acetyl.

Potassium cyanide has but a slight action on the original ether.

Acetyl chloralalcoholate, $CCl_3.CH.(O.C_2H_3O).(O.C_2H_5)$, yields chloroform on treatment with alcoholic potash; and with potassium cyanide, potassium chloride, and dichloracetate, with evolution of hydrocyanic acid. C. F. C.

Nitroso-compounds of the Fatty Series. By V. MEYER and J. ZÜBLIN (*Deut. Chem. Ges. Ber.*, xi, 320—324).—An acid body is formed by the action of nitrous acid upon acetoacetic ether, as Meyer has already shown, the reaction being:—

$$C_6H_{10}O_3 + HNO_2 = H_2O + C_6H_9O_4N.$$

This acid was originally obtained as a heavy yellowish oil, which did not solidify at − 25°, but a small quantity of it suddenly crystallised, after remaining liquid for months. By means of the crystals thus accidentally obtained, the authors have been enabled to effect the crystallisation of large quantities of the acid. The crystals are hard, shining, colourless prisms, which melt at 52—54° to a transparent liquid, which is completely decomposed by distillation. From the fact that acetyl chloride is without action on this body, the authors infer the absence of the group $=N-OH$, and represent its constitution by the formula, $CH_3.CO.CH(NO).COOC_2H_5$, *i.e.*, *nitrosoacetoacetic* ether, rather than oximidoacetoacetic ether.

Nitrosomethylacetone is obtained by the action of nitrous acid upon methylacetoacetic ether:

$$CH_3.CO.CH(CH_3).COOC_2H_5 + H_2O + NO.OH = H_2O + CO_2 + C_2H_5.OH + CH_3.CO.CH(NO)CH_3.$$

It crystallises from water in pearly scales, and from its solutions in ether, alcohol, and chloroform in colourless prisms, which melt at 74°. It boils without decomposition at 185°; and as the vapour may be heated to 250° without change, the authors have determined its density and obtained the number 3·51, exactly coinciding with that required by the formula, $C_4H_7O_2N$. Nitrosomethylacetone is the first of the nitroso-bodies whose vapour-density has been determined.

Nitrosoethylacetone, $CH_3CO.CH.(NO).C_2H_5$, is obtained in a manner precisely similar to its homologue. It forms colourless crystals, which are easily soluble in alcohol, ether, and chloroform. They melt at 53—55°.

The above compounds are characterised by perfectly similar reactions. With phenol and sulphuric acid they give deep-red solutions; and a fiery saffranine-red colour when they are dissolved in aniline, and glacial acetic acid is added. C. F. C.

Reaction of Acetone with CNK,' CNSK, HCl and H_2O.—By F. URECH (*Deut. Chem. Ges. Ber.*, xi, 467—469).—The author has already stated (*Ber.*, vi, 1117) that the compound, $C_5H_7NO_2S$, is formed in this reaction. It is a white crystalline body, which melts at 152°, and when heated with concentrated HCl at 120°, splits up according to the equation—

$$C_5H_7NO_2S + 3H_2O + HCl = (CH_3)_2COH.CO.(OH) + NH_4Cl + SH_2 + CO_2.$$

By heating the aqueous solution of the compound $C_5H_7NO_2S$ with lead acetate, the S-atom is removed, and is replaced by an O-atom. The compound, $C_5H_7NO_3$, thus formed, crystallises in long white prisms, which melt at 73° : it may be distilled unchanged.

On adding silver nitrate to an aqueous solution of $C_5H_7NO_2S$, no silver sulphide is formed, but a crystalline precipitate of the compound $C_5H_6Ag.NO_2S$.

In conclusion, the author discusses the equation by which the original reaction is expressed, viz. :—

$$(CH_3)_2CO + KCN + CNSK + H_2O + 3HCl = C_5H_7NO_2S + 2KCl + NH_4Cl.$$

C. F. C.

Dipyrotartracetone, a Product of the Action of Heat on Tartaric Acid. By E. BOURGOIN (*Compt. rend.*, lxxxvi, 674—676).—The author has isolated from the liquid product which is always formed, in small quantity, in the decomposition of tartaric acid by heat, a body boiling at 230°, having the empirical formula, C_4H_6O, but a vapour density corresponding with the doubled formula, $C_8H_{12}O_2$. Dipyrotartracetone is a colourless liquid of a strong aromatic odour, very slightly soluble in water, but readily soluble in alcohol, ether, carbon bisulphide, and chloroform: its density is about the same as that of water. It combines readily with bromine, but the author did not succeed in obtaining any compounds with alkaline bisulphites. This compound appears to be derived from 2 mol. pyrotartaric acid, thus:

$$2C_5H_8O_4 = C_8H_{12}O_2 + 2CO_2 + 2H_2O.$$

That such is the actual derivation of this compound, and that its construction is that of a dipyrotartracetone, the author will subsequently show. C. F. C.

Formation of α-Dichloropropionic Acid from Pyroracemic Acid. By H. BECKURTS and R. OTTO (*Deut. Chem. Ges. Ber.*, xi, 386—391).—*The chloride of α-dichloropropionic acid*, obtained by the action of 2 molecules of phosphorous chloride on 3 molecules of α-dichloropropionic acid, boils between 105° and 115°, and is decomposed by water into α-dichloropropionic acid, by alcohol into an ether boiling at 155—160°, and by ammonia into an amide melting at 116—117°.

The chloride can also be prepared by acting on α-dichlorpropionic acid with phosphoric chloride, but it cannot be separated from the phosphorus oxychloride by distillation on account of the closeness of their boiling-points.

When phosphoric chloride acts on pyroracemic acid, hydrochloric acid, carbon monoxide and carbonic anhydride are evolved, and apparently some acetyl chloride, whilst a mixture of phosphorus oxychloride and the chloride of α-dichloropropionic acid distils over between 100° and 130°, leaving in the retort a large quantity of a syrupy liquid. The chloride of α-dichloropropionic acid was identified by conversion into ethyl dichloropropionate (b.-p. 155—160°), and into the amide (m.-p. 116°): 60 grams of α-pyroracemic acid only yielded 13·2 grams of ethyl dichloropropionate. The author considers that the action of phosphoric chloride on pyroracemic acid cannot be regarded merely as a substitution of Cl_2 for O, and that therefore the formation of α-dichloropropionic acid does not necessarily prove that pyroracemic is a ketonic acid having the structure $CH_3.CO.COOH$.

W. C. W.

Normal Ethyloxybutyric Acid and its Derivatives. By E. Duvillier (*Compt. rend.*, lxxxvi, 47).—When normal ethyl bromobutyrate is treated with sodium ethylate in alcoholic solution, an ether is obtained which, on purification, boils at 168—174°. It is insoluble in water and lighter than that liquid, has an agreeable odour, and is soluble in all proportions in alcohol and ether: this body has the composition of ethylic ethyloxybutyrate,—

$$CH_3.CH_2.CH(OC_2H_5).CO.OC_2H_5.$$

Ethylic ethyloxybutyrate is easily saponified by potassium hydrate, and from the solution, the potassium salt of ethyloxybutyric acid may be obtained as a deliquescent salt very soluble in water and in alcohol. With sulphate of zinc this salt yields the zinc salt, as an uncrystallisable resinous mass, which, on treatment with sulphuretted hydrogen, gives the free acid, $CH_3.CH_2.CH(OC_2H_5).COOH$, as an oily liquid, soluble in all proportions in water, alcohol, and ether. On neutralising this acid with baryta-water, an uncrystallisable barium salt is obtained, soluble in water and in alcohol: other salts may be prepared from it by double decomposition with the sulphates; they are all very soluble in water and in alcohol. The silver salt crystallises in nodules, which decompose rapidly when heated; it is quickly blackened on exposure to light.

Ethyl bromovalerate treated in a similar way, yields ethylic ethyloxyvalerate. The principal ethyloxyvalerates may be obtained in the same way as the corresponding ethyloxybutyrates. They are soluble in water and extremely soluble in alcohol. The zinc salt is a slightly soluble resinous mass, melting in hot water to a viscid liquid, which solidifies on cooling. It is soluble in ether.

The author has also obtained thioxybutyric and thioxyvaleric acids, by adding to a concentrated aqueous solution of potassium sulphydrate, either bromobutyric or bromovaleric acid, separating the potassium bromide, acidifying with dilute sulphuric acid, and separating the acid by means of ether; after removal of the ether, the acids are boiled with water for some time to remove butyric and valeric acids.

Thio-oxybutyric acid is a viscous substance, soluble in all proportions in water, alcohol, and ether. Thioxyvaleric acid is scarcely soluble even in hot water, soluble in all proportions in alcohol and ether; when heated it forms a viscid liquid becoming nearly solid on cooling. Both these acids have a repulsive odour.

The salts of these two acids closely resemble one another. The alkali-salts are very soluble, those with the alkaline-earths less so; the rest are insoluble. These two acids and their salts have the greatest resemblance to Claesson's thioglycollic acid and its salts.

C. W. W.

The Chemical Nature of Mesoxalic Acid, and Preparation of Tartronic Acid. By PETRIEFF (*Deut. Chem. Ges. Ber.*, xi, 414—417).—Deichsel's research on the mesoxalates favours the hypothesis that mesoxalic acid is dihydroxymalonic acid, $C(OH)_2(COOH)_2$, and not a ketonic acid, $CO(COOH)_2$. The ammonium salt, however, appeared to contain a molecule of water less than the other mesoxalates. Petrieff finds that by saturating an aqueous solution of mesoxalic acid with ammonium carbonate, and evaporating the liquid in a vacuum, the ammonium mesoxalate is obtained in colourless needles, analogous in composition to the other salts of this acid. Deichsel's salt, which was formed by saturating an alcoholic solution of mesoxalic acid with ammonia, is probably the amide of the acid ethyl mesoxalate. Ammonium mesoxalate undergoes no change on exposure to the air; it is easily soluble in water, but with difficulty in alcohol.

The existence of two hydroxyls united to the same atom of carbon, in mesoxalic acid, is evident from the formation of *ethyl-diacetatomesoxalate* by the action of 2 molecules of acetyl chloride on 1 molecule of mesoxalic acid. This ether crystallises in colourless needles, which melt with partial decomposition at 145°.

Diacetatomesoxalic acid, prepared by the action of dilute alcoholic potash on the preceding compound, crystallises in needles which melt at 130°, and decompose at a higher temperature. Mesoxalic acid is identical in every respect with the dioxymalonic acid prepared from dibromomalonic acid.

The author obtained *tartronic* or *oxymalonic acid* by the action of silver oxide on monobromomalonic acid prepared by the reduction of an aqueous solution of dibromo-malonic acid with sodium amalgam. When an alcoholic solution is employed, the acid ethyl monobromomalonate is produced; monobromomalonic acid crystallises in large quadratic plates, which dissolve easily in alcohol, forming the acid ethereal salt. Tartronic acid was also obtained by heating the product of the action of potassium cyanide on dibromacetic acid with potassium hydrate. By the action of sodium amalgam on a dilute aqueous solution of dioxymalonic acid, an acid was formed which seemed to be a mixture of dioxymalonic and tartronic acids.

W. C. W.

Synthesis of Tricarballylic Acid. By G. MIEHLE (*Liebig's Annalen*, cxc, 322—327).—When acetosuccinic ether dissolved in an equal volume of benzene is acted on by sodium, and monochloracetic ether subsequently added, a sharp reaction takes place accompanied by a rise in temperature, and sodium chloride and acetotricarballylic ether are formed. This ether is a yellow oily liquid, which boils between 280° and 300°, but is at the same time decomposed. On treatment with a hot concentrated alcoholic solution of potassium hydrate, it splits up into alcohol and potassium acetate and tricarballylate.

$$CH_3.CO.C(CH_2.COOC_2H_5)_2.COOC_2H_5 + 4KOH = \\ CH(CH_2.COOK)_2.COOK + CH_3.COOK = 3C_2H_5.HO.$$

The potassium salt after purification, was converted into the insoluble lead salt and decomposed by sulphuretted hydrogen, when it yielded tricarballylic acid in anhydrous colourless, short, rhombic prisms, melting at 158°, and very easily soluble in water and alcohol, but only with difficulty soluble in ether. It was thought possible that acetoglutaric acid might be formed on decomposing the acetotricarballylic ether with baryta-water, but on making the experiment no trace of this body was found. E. N.

Conversion of Nitrils into Amides. By A. PINNER and F. KLEIN (*Deut. Chem. Ges. Ber.*, xi, 4—11).—It has been already shown by the authors (*Ber.*, xi, 1889), that when a mixture of a nitril and an alcohol is acted on by gaseous hydrochloric or hydrobromic acid, the following reaction takes place:

$$RCN + ROH + 2HCl = R'O{-}C(R)(Cl)(NH_2).HCl = \\ R'O{-}C(R)(NH).HCl + HCl.$$

By the action of gaseous hydrochloric acid on benzonitrile and isobutylalcohol, the hydrochloride of isobutylbenzimido-ether was prepared, which with alcoholic ammonium yields isobutylbenzimido-ether, $C_4H_9O.C(C_6H_5).NH$, and the hydrochloride of benzimido-amide, $C_6H_5.C(NH).NH_2.HCl$. The free amide was obtained from the latter body by means of a concentrated solution of sodium hydrate.

Benzimidoamide, $C_6H_5C(NH)(NH_2)$, forms a hard white fibrous crystalline mass, melting at 75—80° to an oily liquid. It is moderately soluble in water, readily soluble in ether, and very easily soluble in alcohol. It has an alkaline taste and a strongly alkaline reaction. On heating, it loses ammonia and yields cyaphenine, a polymeride of benzonitril, C_6H_5CN, together with a third body, which appears to be identical with dibenzimidoimide, $C_{14}H_{13}N_3$. With a solution of silver nitrate, the hydrochloride of the amide yields a soluble nitrate of the silver compound, $C_6H_5C(NAg)(NH_2)$, which is precipitated by sodium hydrate as a white mass.

Cyaphenine, which is also formed by the action of ethyl iodide on isobutylbenzimido-ether, crystallises in small needles melting at 231°, and appears to be identical with the compound described by Cloez (*Annalen*, cxv, 27) and Engler (*Annalen*, cxxxiii, 147). It is insoluble in water and hydrochloric acid, nearly insoluble in cold alcohol and ether, soluble with great difficulty in hot alcohol, but easily soluble in hot ethyl iodide.

Ethylbenzimidoamide, $C_6H_5.C(NC_2H_5)(NH_2)$, is an oily liquid, with strongly basic properties, its hydrochloride forming a fine crystalline compound with platinum chloride. The hydriodide is obtained by the action of ethyl iodide on benzimidoamide.

Dibenzimido-imide, $\{C_6H_5.C.(NH).\}_2(NH)$, forms large colourless needles melting at 108—109°. It is formed by boiling benzimidoamide with four or five times its weight of acetic anhydride.

Benzimidoacetate, $C_6H_5.C.(NH)(OC_2H_3O)$, is formed by boiling isobutylbenzimido-ether with acetic anhydride, and forms a mass of long delicate needles, melting at 116°. It is insoluble in water and dilute acids, but easily soluble in alcohol and ether. E. N.

On Brominated Benzenesulphonic Acids. Hy H. LIMPRICHT (*Liebig's Annalen*, cxci, 175—253).—The researches of Reinke and Knuth (*Annalen*, clxxxvi, 272 and 290) rendered it probable that the tribromobenzenesulphonic acid formed by the action of sulphuric acid on symmetrical tribromobenzene is identical with that obtained from tribromometamidobenzenesulphonic acid. To remove all doubt on this point the author, in co-operation with Langfurth and Bässmann, has made a fresh examination of the acids obtained by both reactions, and of many of their derivatives.

I. BROMINATED DERIVATIVES OF METAMIDOBENZENESULPHONIC ACID.—The only products of the action of bromine on the metamido-acid heretofore obtained are the dibromo- and tribromo-derivatives. Langfurth finds, however, that on adding one mol. of bromine to a cold very dilute solution of the amido acid the following body is also formed.

Monobromamidobenzesulphonic acid, $C_6H_3.SO_3H:NH_2:Br\ (= 1:3:4)$.—This acid, which is also formed by heating the dibromo acid with hydrochloric acid and phosphorus, crystallises either in delicate anhydrous needles or in large four- or six-sided prisms, containing 1 mol. of water. It dissolves freely in hot water, and sparingly in alcohol. The following salts have been analysed.—

$C_6H_3Br\ (NH_2)\ SO_3K + 1·5H_2O$ crystallises in laminæ, very easily soluble in water.

$[C_6H_3Br(NH_2)SO_3]_2Ba,H_2O$ or $3H_2O$. Scaly nodules, very easily soluble in water.

$[C_6H_3Br(NH_2)SO_3]Pb,\ 0·5H_2O$(?). Easily soluble needles, the solution of which turns red on standing.

By treatment with nitrous acid, the acid is converted into the *diazo-compound*, $C_6H_3BrSO_3N_2$, which when boiled with strong hydrobromic acid yields—

Dibromobenzenesulphonic Acid, $C_6H_3.SO_3H : Br : Br\ (=1:3:4)$.—This substance yields by the ordinary reactions a *chloride* identical with that of Limpricht and Göslich, and an *amide* crystallising in white needles, which melt at 175°.

Dibromamidobenzenesulphonic Acid, $C_6H_2.SO_3H : NH_2 : Br : Br\ (=1:3:4:6)$.—Berndsen prepared this acid by treating metamidobenzenesulphonic acid with 2 mols. of bromine. Afterwards Reinke and Knuth obtained it by treating tribromonitrobenzenesulphonic acid with tin and hydrochloric acid. Langfurth finds that it is easily produced by heating tribromamidobenzenesulphonic acid at 150° with water, when an exchange of one atom of bromine for hydrogen takes place. It is converted by boiling with alcohol and nitrous acid into—

Dibromobenzenesulphonic acid, $C_6H_3.SO_3H : Br : Br$ (= 1 : 4 : 6).—This acid crystallises in white deliquescent needles, which melt at 80°, giving off water of crystallisation. The anhydrous acid melts at 110°. When heated at 180° with hydrobromic acid it is resolved into sulphuric acid and metadibromobenzene. The following salts have been analysed; they are all soluble in water:—

$C_6H_3Br_2SO_3NH_4$. White needles.

$C_6H_3Br_2SO_3K$. Colourless thin laminæ, or yellow rhombic tables.

$(C_6H_3Br_2SO_3)_2Ba.2H_2O$. Long prisms, or thin white laminæ.

$(C_6H_3Br_2SO_3)_2Ca.3H_2O$. Aggregated white laminæ or needles.

$(C_6H_3Br_2SO_3)_2Pb.3H_2O$. Short yellow prisms with truncated angles.

$C_6H_3Br_2SO_3Ag$. Colourless pointed prisms collected in nodules, which rapidly darken in the light. Its solutions are very unstable.

The acid yields by the ordinary reactions a *chloride* crystallising in rhombic prisms, which melt at 79°, and an *amide* crystallising in white needles, and melting at 190°.

Tribromobenzenesulphonic Acid, $C_6H_3.SO_3H : Br : Br : Br$ (=1 : 3 : 4 : 6).—Langfurth prepares this acid by heating dibromamidobenzenesulphonic acid with acetic and hydrobromic acids and potassium nitrite. It crystallises with 3 mols. of water in needles which melt at 80°. The anhydride melts at 140°. When heated to 200° with hydrobromic acid it is resolved into sulphuric acid and tribromobenzene, melting at 44°, and identical with that described by Körner, whose formula (1 : 2 : 4) is thus confirmed. The following salts, which are all soluble in water, were analysed:—

$C_6H_2Br_3SO_3NH_4.H_2O$. Tufts of white needles.

$C_6H_2Br_3SO_3K.H_2O$. Groups of long needles.

$(C_6H_2Br_3SO_3)_2Ba.3H_2O$. Transparent rhombic tables, or small prisms.

$(C_6H_2Br_3SO_3)_2Ca.6H_2O$. Groups of delicate white needles.

$(C_6H_2Br_3SO_3)_2Pb.4H_2O$. Tufts of white needles.

$C_6H_2Br_3SO_3Ag$. Stellate groups of short needles, quickly turning brown in the light.

The corresponding *chloride* crystallises from ether in large colourless tables, which melt at 86·5°. The *amide* crystallises from alcohol in laminæ, melting above 225°.

Tribromamidobenzenesulphonic Acid, $C_6H.SO_3H : Br : NH_2 : Br : Br$ (=1 : 2 : 3 : 4 : 6).—This acid is obtained by the action of bromine on metamidobenzenesulphonic acid. It was previously prepared by Berndsen, and by Beckurts and Knuth, most of whose statements respecting it have been verified by Langfurth. It is converted by treatment with nitric acid into the *diazo-compound*, which when boiled with alcohol yields—

Tribromobenzenesulphonic Acid, $C_6H_2.SO_2H : Br : Br : Br$ (=1 : 2 : 4 : 6).—This acid crystallises in six-sided tables, which melt at 95°. When heated at 180° with strong hydrochloric acid it yields symmetrical tribromobenzene, melting at 118·5°. The following salts were analysed:—

$C_6H_2Br_3SO_3NH_4.H_2O$. Feathery groups of rhombic tables, easily soluble.

$C_6H_2Br_3SO_3K.H_2O$. Thin plates or rhombic tables, efflorescent in the air.

$(C_6H_2Br_3SO_3)_2Ba$. Large thin six-sided laminæ with $9H_2O$, or short rhombic prisms with $2H_2O$, soluble in water.

$(C_6H_2Br_3SO_3)_2Ca.8H_2O$. Brilliant white quadratic tables.

$(C_6H_2Br_3SO_3)_2Pb.9H_2O$. Long white prisms and laminæ, easily soluble in hot water.

The *chloride*, $C_6H_2Br_3.SO_2Cl$, crystallises from ether in colourless rhombic plates, melting at 64—65°. The *amide*, $C_6H_2Br_3SO_2.NH_2$, forms very delicate needles, which decompose at 220° without melting.

Pure tribromobenzenesulphonic acid, when heated with concentrated nitric acid, yields a large quantity of nitrotribromobenzene (which crystallises in colourless monoclinic prisms, melting at 124—125)°, together with the following acid:—

Nitrotribromobenzenesulphonic Acid, $C_6H.SO_3H : Br : NO_2 : Br : Br$ ($= 1 : 2 : 3 : 4 : 6$). This acid is very easily soluble in water and alcohol, and crystallises with difficulty in deliquescent prisms containing $2H_2O$.

$C_6H(NO_2)Br_3SO_3K$ forms groups of long needles.

$[C_6H(NO_2)Br_3SO_3]_2Ba.H_2O$ crystallises in white laminæ.

$[C_6H(NO_2)Br_3SO_3]_2Pb.9H_2O$ forms brittle needles and laminæ, sparingly soluble in water.

The *chloride*, $C_6H(NO_2)Br_3.SO_2Cl$, crystallises in small rhombic tables, melting at 144—145°. The *amide*, $C_6H(NO_2)Br_3SO_2.NH_2$, crystallises in microscopic needles, which dissolve very sparingly in water, and soften at 175°.

The free acid, when treated with tin and hydrochloric acid, yields much amidodibromobenzenesulphonic acid, as previously observed by Knuth. The amidotribromo-acid produced at the same time is identical with that formed by the action of 3 mols. of bromine on metamidobenzenesulphonic acid.

Tetrabromobenzenesulphonic Acid, $C_6H.SO_3H : Br : Br : Br : Br$ ($= 1 : 2 : 3 : 4 : 6$).—This acid was obtained by boiling the diazo-compound of tribromamidobenzenesulphonic acid with hydrobromic acid. It crystallises with $5H_2O$ in stellate groups of small white needles, which dissolve easily in water and alcohol, and melting without decomposition. When heated to 150° with strong hydrobromic acid it breaks up into sulphuric acid and tetrabromobenzene (1 : 2 : 3 : 5), which crystallises from alcohol in long white needles, melting at 98·5°.

$C_6HBr_4SO_3K$ forms tufts of white needles or prisms.

$(C_6HBr_4SO_3)_2Ba.1\frac{1}{2}H_2O$ forms thin laminæ and short needles, sparingly soluble in water.

$(C_6HBr_4SO_3)_2Ca.8H_2O$ forms tufts of delicate needles.

$C_6HBr_4SO_2Cl$ crystallises in transparent rhombic tables, melting at 96°.

$C_6HBr_4SO_2.NH_2$ crystallises from alcohol in microscopic needles, which dissolve sparingly in water.

Nitrotetrabromobenzenesulphonic Acid, $C_6.SO_3H:Br:Br:Br:NO_2:Br$ (= 1 : 2 : 3 : 4 : 5 : 6), is formed on heating the preceding acid with concentrated nitric acid. It dissolves easily in water and alcohol, crystallises in needles containing $4H_2O$, and melts without decomposition. When heated to 200° with strong hydrochloric acid, it breaks up into sulphuric acid and *nitrotetrabromobenzene*, melting at 96°.

$C_6(NO_2)Br_4SO_3K.1\frac{1}{2}H_2O$ crystallises in long thin laminæ and prisms.

$[C_6(NO_2)Br_4SO_3]_2Ba.9H_2O$ forms efflorescent prisms and laminæ.

The *chloride*, $C_6(NO_2)Br_4.SO_2Cl$, crystallises from ether in small white needles, melting at 147·5°.

The *amide*, $C_6(NO_2)Br_4SO_2.NH_2$, forms a white crystalline powder, sparingly soluble in water.

The free acid is converted by treatment with tin and hydrochloric acid into the corresponding—

Amidotetrabromobenzenesulphonic Acid.—This substance crystallises in slender needles containing $2H_2O$, and dissolving easily in water and alcohol. Its diazo-compound forms microscopic tables, which explode violently when heated; when evaporated with concentrated hydrobromic acid it yields—

Pentabromobenzenesulphonic acid, $C_6Br_5.SO_3H$, which crystallises in anhydrous needles, sparingly soluble in water.

$C_6Br_5SO_3K.H_2O$ forms small white prisms, sparingly soluble in water.

The *chloride*, $C_6Br_5.SO_2Cl$, crystallises in nodules made up of needles, which melt at 97°.

The *amide*, $C_6Br_5SO_2.NH_2$, also forms slender white needles, which dissolve sparingly in water, more easily in alcohol: it decomposes at 250°.

II. SULPHONIC ACIDS OF SYMMETRICAL TRIBROMOBENZENE AND THEIR DERIVATIVES.—*Tribromobenzene*, $C_6H_3Br_3$ (1 : 3 : 5).—Bässmann obtains this substance in large quantity by dissolving tribromaniline in 95 per cent. alcohol, and adding to the hot solution first a concentrated aqueous solution of potassium nitrite, and then gradually dilute sulphuric acid to acid reaction. The product after distillation melts at 118·5°.

Tribromobenzenesulphonic Acid, $C_6H_2.SO_3H:Br:Br:Br$ (= 1:2:4:6). —This acid, as obtained by the action of sulphuric acid on symmetrical tribromobenzene, crystallises in large transparent rhombic prisms and six-sided tables, containing 1 mol. of water. It is very hygroscopic, dissolves in all proportions of water and alcohol, and melts at 95°. Its *salts*, *chloride* and *amide*, agree in characters with those described above. The free acid, when dried and gently heated with concentrated nitric acid, yields besides some nitrotribromobenzene (m.-p. 125°)—

Nitrotribromobenzenesulphonic acid, $C_6H.SO_3H:Br:NO_2:Br:Br$ (= 1 : 2 : 3 : 4 : 6), which crystallises from water in prisms containing $2H_2O$. The anhydrous acid melts at 202°. When heated at 180° with fuming hydrochloric acid it is resolved into sulphuric acid and nitrotribromobenzene, melting at 125°. Its *salts*, *chloride* and *amide*, are identical with those described above. The acid yields by reduction with tin and hydrochloric acid a mixture of amidodibromo- and amidotribromo-benzenesulphonic acids. The latter is converted by treatment with nitrous acid into the *diazo-compound*, $C_6HBr_3SO_3N$, which, when boiled with hydrobromic acid gives off nitrogen, and yields a tetrabromobenzenesulphonic acid identical with that described above by Langfurth. This acid when heated at 200° for some time breaks up into sulphuric acid and *tetrabromobenzene* (1 : 2 : 3 : 5), which forms with sulphuric acid a sulphonic acid identical with that from which it was derived.

The amidodibromobenzenesulphonic acid formed in the reduction of the nitrotribromo-acid by tin and hydrochloric acid, as just described, yields by treatment with alcohol and potassium nitrite a yellow crystalline compound (the *potassium salt of the diazo-acid*), which on addition of dilute sulphuric acid yields the free diazo acid in the form of a greyish-white heavy precipitate, consisting of colourless microscopic prisms. The constitution of this body is still under investigation. When heated with alcohol and nitrous acid it is converted into the dibromobenzenesulphonic acid before described.

Nitrodibromobenzene Sulphonic Acid, $C_6H_2.SO_3H : NO_2 : Br : Br$ (= 1 : 3 : 4 : 6).—This acid is formed on treating dibromobenzenesulphonic acid with the strongest nitric acid. It crystallises in small needles and prisms, which dissolve easily in water.

$C_6H_2(NO_2)Br_2SO_3K$ forms concentric groups of yellowish needles or prisms.

$[C_6H_2(NO_2)Br_2SO_3]_2Ba.H_2O$ crystallises in stellate groups of delicate prisms.

$[C_6H_2(NO_2)Br_2SO_3]_2Ca.6H_2O$ forms deliquescent prisms and six-sided laminæ, easily soluble.

$[C_6H_2(NO_2)Br_2SO_3]Pb.4H_2O$ forms easily soluble brilliant laminæ.

$C_6H_2(NO_2)Br_2.SO_2Cl$ crystallises from ether in quadratic prisms and tables, melting at 115·5°.

$C_6H_2(NO_2)Br_2.SO_2.NH_2$ dissolves easily in hot water and alcohol, and crystallises in small rhombic tables, which do not melt at 240°.

The acid yields by reduction with stannous chloride the corresponding *amido-acid*, which is identical with that described by Langfurth.

Dinitrotribromobenzenesulphonic acid, $C_6.SO_3H : Br : NO_2 : Br : NO_2 : Br$ (= 1 : 2 : 3 : 4 : 5 : 6), is formed on heating tribromobenzenesulphonic acid (1 : 2 : 4 : 6) with excess of the strongest nitric acid. It crystallises in beautiful long colourless prisms, which dissolve easily in water and alcohol. It undergoes decomposition when heated at 230° with water.

$C_6(NO_2)_2Br_3SO_3NH_4$ crystallises in short prisms, easily soluble in water.

$C_6(NO_2)_2Br_3SO_3K.H_2O$ forms white prisms and six-sided laminæ, or short four-sided prisms.

$[C_6(NO_2)_2Br_3SO_3]_2Ba.9H_2O$ forms brilliant white laminæ, efflorescent in the air.

$[C_6(NO_2)_2Br_3SO_3]_2Ca.7\frac{1}{2}H_2O$ crystallises in dazzling-white rhombic laminæ.

$[C_6(NO_2)_2Br_3SO_3]_2Pb.9H_2O$ forms nacreous white rhombic laminæ, which effloresce in the air, and dissolve sparingly in cold water.

$C_6(NO_2)_2Br_3.SO_2Cl$ crystallises in transparent six-sided rhombic tables, melting with decomposition at 203°.

$C_6(NO_2)_2Br_3.SO_2.NH_2$ dissolves sparingly in water, easily in alcohol. It crystallises in white matted needles, which melt at 255—260°.

The free acid, when treated with stannous chloride, is for the most part converted into a mixture of diamidomonobromo- and diamidodibromo-benzenesulphonic acids, the former preponderating.

Diamidomonobromobenzenesulphonic acid, $C_6H_2.SO_3H : NH_2 : Br : NH_2$ ($= 1 : 3 : 4 : 5$), crystallises in long white silky needles. Its salts are all easily soluble and difficult to crystallise; their solutions assume a blood-red colour on evaporation.

Diamidodibromobenzenesulphonic acid, $C_6H.SO_3H : NH_2 : Br : NH_2 : Br$ ($= 1 : 3 : 4 : 5 : 6$), forms white rhombic tables, which are very sparingly soluble, and gradually acquire a yellow colour in the air.

The results of the foregoing investigations establish the identity of the tribromobenzenesulphonic acid obtained from tribromometamidobenzenesulphonic acid by substitution of H for NH_2 with that formed by the action of sulphuric acid on symmetrical tribromobenzene. The formula of this acid being $C_6H_2.SO_3H : Br : Br : Br$ ($= 1 : 2 : 4 : 6$) it is obviously capable of yielding only one nitro- and one amido-derivative, and only one tetrabromo-derivative: these must have the following constitution:—

Nitro-derivative	$C_6H_2.SO_3H : Br : NO_2 : Br : Br$ ($= 1 : 2 : 3 : 4 : 6$)
Amido-derivative......	$C_6H_2.SO_3H : Br : NH_2 : Br : Br$ ($= 1 : 2 : 3 : 4 : 6$)
Tetrabromo-derivative	$C_6H_2.SO_3H : Br : Br : Br : Br$ ($= 1 : 2 : 3 : 4 : 6$)

The two latter acids were previously examined by Beckurts, *Annalen*, clxxvi, 214), who assigned to them a different constitution, which cannot now be maintained.

Limpricht calls attention to the following generalisations with regard to the positions taken by bromine atoms entering into molecules of the amidobenzenesulphonic acids.

In orthamidobenzenesulphonic acid the first atom of bromine takes the para-position in relation to the NH_2-group; the second atom of bromine takes the meta-position in relation to the first, and the third takes the meta-position in relation to the other two, displacing SO_3H, and forming tribromaniline. Thus:

Ortho-acid.

	1.	2.	3.	4.	5.	6.
C_6	SO_3H	NH_2	H	H	H	H
C_6	SO_3H	NH_2	H	H	Br	H
C_6	SO_3H	NH_2	Br	H	Br	H
C_6	Br	NH_2	Br	H	Br	H

In metamidobenzenesulphonic acid the first atom of bromine takes the ortho-position in relation to the NH_2-group; the second atom again takes the meta-position in relation to the first; and the third takes the meta-position in relation to the other two. The further action of bromine results in the formation of bromanil.

Meta-acid.

	1.	2.	3.	4.	5.	6.
C_6	SO_3H	H	NH_2	H	H	H
C_6	SO_3H	H	NH_2	Br	H	H
C_6	SO_3H	H	NH_2	Br	H	Br
C_6	SO_3H	Br	NH_2	Br	H	Br

In the case of paramidobenzenesulphonic acid no monobrominated derivative is yet known. The constitution of the di- and tri-brominated derivatives is shown below:—

Para-acid.

	1.	2.	3.	4.	5.	6.
C_6	SO_3H	H	H	NH_2	H	H
C_6	SO_3H	H	Br	NH_2	Br	H
C_6	Br	H	Br	NH_2	Br	H

In all cases, therefore, the positions of the second and third bromine-atoms are determined by that of the first, the second always taking the meta-position in relation to the first, and the third taking the meta-position in relation to both the first and second. And this holds true even when the position of the third atom is already occupied by the group SO_3H, the latter being replaced by bromine, with consequent formation of tribromaniline. J. R.

Action of Carbonyl Chloride on Xylene in Presence of Aluminium Chloride. By E. Ador and A. Rilliet (*Deut. Chem. Ges. Ber.*, xi, 399).—Carbonyl chloride is passed through xylene cooled down to $-15°$. On adding aluminium chloride to the liquid, a ketone is formed, which boils at 340° and does not solidify at $-60°$. By boiling the ketone with potassium hydrate solution, an acid is obtained having the formula $C_6H_3(CH_3)_2.COOH$, which on oxidation yields two acids, viz., $C_6H_3(CH_3)(COOH)_2$ and $C_6H_3(COOH)_3$.

By long continued boiling the ketone is decomposed into water and a hydrocarbon, thus: $C_{17}H_{18}O - H_2O = C_{17}H_{16}$. Tolyl ketone behaves in a similar manner. W. C. W.

Azophenols. By P. Weselsky and R. Benedikt (*Deut. Chem. Ges. Ber.*, xi, 398).—Mononitrophenols are converted into azophenols by fusion with potassium hydrate. Ortho-azophenol prepared by means of this reaction crystallises in golden scales, which melt at 171°, and are volatile without decomposition. The crystals dissolve in ether and alcohol, but are insoluble in water, so that the unattacked nitrophenol is easily removed by washing with water.

W. C. W.

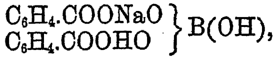
Nitro-derivatives of the Hydroquinones. By R. NIETZKI (*Deut. Chem. Ges. Ber.*, x, 469—472).—The author has prepared the dinitro-derivative $C_6H_4(NO_2)_2O_2$ indirectly by nitrating diacetylhydroquinone and eliminating the acetyl groups by dissolving the nitro-compound thus formed in a dilute alkali. It crystallises in flat golden-yellow needles, which melt at 135°, and appears to be identical with the compound which Strecker obtained (*Annalen*, cxviii, 293) by the action of dilute acids upon dinitro-arbutin. It possesses strongly acid properties, and forms metallic derivatives which are for the most part easily soluble. The barium compound, however, $C_6H_2(NO_2)_2BaO_2$, is almost insoluble in water. On mixing aqueous solutions of dinitro-hydroquinone and barium hydrate, it is obtained in slender needles, which are almost black. C. F. C.

Action of Bromine on Phloroglucin. By R. BENEDIKT (*Chem. Centr.*, 1878, 101—103).—*Phlorobromine*, C_6Br_9HO, is prepared by adding 10 parts of bromine to 1 part of phloroglucin dissolved in water, and leaving the mixture at rest for several hours. By recrystallising the crude product from chloroform, and expelling the excess of bromine by heating with water, the phlorobromine is obtained in colourless rhombic prisms insoluble in water, which melt at 152°, and decompose at a higher temperature. Pentabromacetone (m. p. 76°) and an oily liquid, which has not yet been investigated, separate out when water is added to an alcoholic solution of phlorobromine which has been allowed to stand for some time. Neither nitric acid nor potassium hydrate solution attacks phlorobromine, but it is decomposed by ammonia, forming bromoform and a new substance having the formula $C_5Br_6H_4N_2$. This compound dissolves in water, yielding a neutral solution. It is deposited from a boiling aqueous solution in white opaque crystals, melting at 120°, and subliming without decomposition. It yields a brominated acid when treated with dilute sulphuric acid at 120°. The author finds, contrary to the statement of Cloez, that pentabromacetone is readily converted into dibromacetamide by *aqueous* ammonia. Treated by Beckurts and Otto's method, it is converted almost quantitatively into dibromacetic acid.

W. C. W.

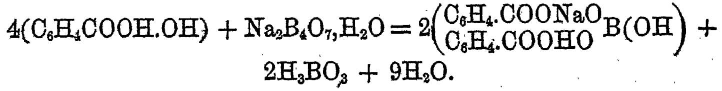
On Sodium Compounds of Salicylic Acid. By E. HOFMANN (*Arch. Pharm.* [3], xii, 226—229).—If a solution of sodium salicylate containing free salicylic acid be kept for some time, large clear hard crystals separate. These become opaque on the addition of water, being converted into pseudomorphs of salicylic acid. They appear to be an acid sodium salicylate, $C_7H_5O_3Na + C_7H_6O_3$, which by water are resolved into sodium salicylate and free salicylic acid. They are, however, soluble without decomposition in alcohol, and may easily be prepared by evaporating an alcoholic solution of the acid and the sodium salt. The corresponding potassium, lithium, and ammonium compounds have been prepared. E. W. P.

Behaviour of Borax to Salicylic Acid and of Boric Acid to Salicylates. By E. JAHNS (*Arch. Pharm.* [3], xii, 212—226).—It appears that the solution of salicylic acid in borax solution is no simple solution, but contains a compound, which can be crystallised from its solutions, and has the composition $C_{14}H_{10}O_5NaBO_2$. If 4 mols. of salicylic acid are dissolved in a boiling solution containing 1 mol. of borax in about 5 parts of water, the solution on cooling first deposits boric acid unaltered, and then the compound



$$\left.\begin{array}{l}C_6H_4.COONaO\\C_6H_4.COOHO\end{array}\right\}B(OH),$$

analogous to the borotartrate. The reaction therefore takes place according to the equation—



$$4(C_6H_4COOH.OH) + Na_2B_4O_7,H_2O = 2\left(\begin{array}{l}C_6H_4.COONaO\\C_6H_4.COOHO\end{array}B(OH\right) + 2H_3BO_3 + 9H_2O.$$

Free borosalicylic acid has not as yet been obtained, but several of its salts are described, and the analogies between borosalicylic and borotartaric acids are pointed out. E. W. P.

Derivatives of Methyl-protocatechuic Acid. By KAETA AKIMORI MATSMOTO (*Deut. Chem. Ges. Ber.*, xi, 122—141).—The author gives historical notices of veratric acid (dimethyl-protocatechuic acid) $C_6H_3(OCH_3)_2.COOH$ (3 : 4 : 1) (m. p. 174—175°), of vanillic acid, $C_6H_3(OCH_3)OH.COOH$ (3 : 4 : 1) (m. p. 107°), and of isovanillic acid, $C_6H_3(OH)(OCH_3).COOH$ (3 : 4 : 1).

To prepare isovanillic acid, protocatechuic acid is heated with potassium hydrate, methyl iodide, and methyl alcohol in sealed tubes at 150—170°; the methyl ethers of veratric, pyrocatechuic, and isovanillic acids are formed. The product is heated with potassium hydrate and ether, the latter removing the veratric acid, whilst the potash retains the other two acids in solution. The alkaline solution on boiling yields the potassium salts, and when the solution cools, potassium isovanillate separates out, the protocatechuate remaining in solution. Another method is to heat veratric acid with hydrochloric acid in sealed tubes at 160—170° (for 2 grams veratric acid 75 c.c. of dilute HCl, consisting of 1 part of HCl, sp. gr. 1·20, to 2 parts of water). The end of the reaction is ascertained by the crystals which separate out on cooling being transparent. The isovanillic acid is purified by boiling with acetic acid, the acetisovanillic acid separating out when the product is poured into water, whilst the veratric acid remains in solution. The acetyl-compound yields isovanillic acid when boiled with dilute solution of potassium hydrate. Isovanillic acid crystallises in shining transparent prisms, like those of vanillic acid, and melts at 250°. It is soluble in alcohol and ether. Its aqueous solutions give no reaction with ferric chloride. The alkaline isovanillates are easily soluble in water, and those of barium, calcium, and magnesium are tolerably soluble salts, crystallising in needles. The lead salt is obtained as a difficultly soluble white crystalline precipitate; the silver salt is also white, and is decomposed by light less rapidly than the vanillate.

The following are the solubilities of the three methylated protocatechuic acids in water:—

		Pts. of water, at 14°.	Pts. of water, at 100°.
1 pt. veratric acid......	(m. p. 174—175°)	2100—2150	160—165
1 „ vanillic acid	(„ 207°)	850— 860	39— 40
1 „ isovanillic acid....	(„ 250°)	1650—1700	155—160

The methyl and ethyl ethers of these acids were obtained by passing hydrochloric acid gas through a solution of the acid in the respective alcohols.

Methyl veratrate, $C_6H_3(OCH_3)_2.COOCH_3$, is difficultly soluble in water, easily in ether and alcohol, and crystallises from its alcoholic solution in white needles. It melts at 59—60°, and boils at 300°, is odourless, and not attacked by ammonia or alkalis at the ordinary temperature. This ether may also be prepared by heating potassium hydrate, methyl iodide, and vanillic acid in sealed tubes. The product of the reaction is then shaken up with ether, and the ethereal solution treated with dilute solution of potassium hydrate to remove unaltered vanillic acid.

Ethyl veratrate has already been described by the author and Tiemann (*Ber.*, ix, 942; this *Journal*, 1876, ii, 524).

Methyl vanillate, $C_6H_3(OCH_3)OH.COOCH_3$, crystallises in shining white needles, melting at 62—63°. It boils at 285—287°, and is not attacked by alkalis at the ordinary temperature.

Ethyl vanillate has been described by Tiemann and Mendelsohn (*Ber.*, x, 60).

Methyl protocatechuate, $C_6H_3(OH)_2.COOCH_3$, has been prepared by P. I. Meyer, who has communicated his results to the author. It crystallises in white needles, which melt at 134·5°, and differs from the ethers of the methylated protocatechuic acids by yielding a green colour with ferric chloride.

Ethyl protocatechuate has been prepared by Fittig and Macalpine (*Liebig's Annalen*, clxviii, 113). It crystallises in prisms, and melts at 133—134°.

Acetovanillic acid, $C_6H_3(OCH_3)(OC_2H_3O).COOH$, has been obtained by Tiemann and Nagai (*Ber.*, ix, 937; this *Journal*, 1876, i, 78). It crystallises in shining needles, and melts at 142°.

Acetisovanillic Acid, $C_6H_3(OC_2H_3O)(OCH_3).COOH$.—This compound, whose preparation is described under the preparation of isovanillic acid, crystallises from alcohol in shining scales, which melt at 206—207°. It is difficultly soluble in water, more easily, however, in alcohol and ether.

Nitro-derivatives of Methylated Protocatechuic Acids.—The author, in conjunction with Tiemann (*Ber.*, ix, 937; this *Journal*, 1876, ii, 524) has already described the preparation of several of these derivatives.

Methyl nitroveratrate, $C_6H_2NO_2(OCH_3)_2.COOCH_3$, is prepared from nitro-veratric acid. It is difficultly soluble in water and alcohol, but dissolves easily in boiling alcohol and ether. It crystallises in small needles, which melt at 143—144°.

Nitro-acetisovanillic acid, $C_6H_2NO_2(OC_2H_3O)(OCH_3).COOH$, is prepared by nitrating acetisovanillic acid. It crystallises in transparent shining needles, melting at 168—169°. It dissolves with difficulty in cold water, more easily in hot water, and is soluble in alcohol and ether.

Nitro-isovanillic acid, $C_6H_2NO_2(OH)(OCH_3).COOH$, is obtained by boiling the last-mentioned compound with potassium hydrate. It is easily soluble in hot water, alcohol, and ether, and crystallises in shining needles united in globular masses, and melts at 172—173°.

To discover whether the nitro-group occupies the same position in the above-described nitro-veratric and nitro-acetovanillic acids, the author prepared the methyl-ether of a nitrodimethyl-protocatechuic acid from nitrovanillic acid as follows. 1 mol. of the acid, 2 mols. of KHO, and 2 mols. of CH_3I are heated together in sealed tubes at 110—120°, the product is exhausted with ether, and the ethereal solution treated with dilute alkali to remove nitrovanillic acid. On evaporation, the ethereal solution yields a methyl-nitrodimethyl protocatechuate, which crystallises in hard shining needles, and melts at 127—128°, whilst methyl-nitroveratrate melts at 143—144°. This ether yields, on saponifying, isonitro-dimethyl-protocatechuic acid, $C_6H_2(NO_2)(OCH_3)_2.COOH$, which crystallises in white needles, and melts at 200—202°, whilst its isomeride nitroveratric acid exhibits no constant melting point. Thus it is evident that the acetyl-group in acetovanillic acid exercises some influence on the position taken by the nitro-group in the molecule.

Amido-derivatives.—The author and Tiemann (*op. cit.*) have shown that amido-veratric acid cannot be prepared from the stanno-chloride obtained by reduction of the nitro-acid with tin and hydrochloric acid, owing to its instability. For a similar reason the amido-derivatives of vanillic and isovanillic acids cannot be obtained. Ethyl-amido-veratrate, $C_6H_2(NH_2)(OCH_3)_2.COOC_2H_5$, can, however, be prepared from the ether of the nitro-acid by reduction with tin and hydrochloric acid. It crystallises in small colourless needles, which melt at 88—89°. It is difficultly soluble in water, easily in alcohol and ether, and it forms a hydrochloride with hydrochloric acid. Attempts to obtain the amido-acid by saponification yielded no result.

Bromoveratric acid, $C_6H_2Br(OCH_3)_2.COOH$, is obtained by the action of bromine on an aqueous solution of veratric acid. It crystallises in colourless needles, melting at 183—184°. It is insoluble in cold water, more soluble in hot water, and easily in alcohol and ether.

Dibromo-dimethyl-pyrocatechin (dibromo-veratrol), $C_6H_2Br_2(OCH_3)_2$, is formed at the same time as the bromoveratric acid. It crystallises in shining hard prisms melting at 83—84°. It is insoluble in water, easily soluble in alcohol and ether.

Bromacetovanillic acid, $C_6H_2Br(OH)(OC_2H_3O).COOH$, is prepared by the action of bromine on an aqueous solution of acetovanillic acid; a small quantity of bromovanillic acid and bromoguaiacol are formed at the same time. Bromacetovanillic acid crystallises in shining prisms, which melt at 165—167°. Alcohol and ether dissolve it easily, whilst it is almost insoluble in water.

Bromovanillic acid, $C_6H_2Br(OCH_3)(OH).COOH$, is obtained from the last-mentioned acetyl-compound by boiling with dilute potassium hydrate. It is more soluble in water than the acetyl-compound, dissolves also in alcohol and ether. From its aqueous solutions it separates out in shining needles, which contain 1 mol. of water of crystallisation, which it loses on heating to 100°. The dried compound melts at 193—194°.

The bromoveratric acid prepared from bromovanillic acid by heating it with potassium hydrate, methyl iodide, and methyl alcohol in sealed tubes, and saponifying the ether, is identical with that prepared from veratric acid directly. Thus the acetyl group in acetovanillic acid exercises no such influence on the entrance of the bromine into the molecule as it has shown to exercise upon that of the nitro-group.

Bromoveratric acid fused with potassium hydrate yields pyrogallol, $C_6H_3(OH)_3$, which Barth has already prepared similarly from monobromoprotocatechuic acid (*Annalen*, cxlii, 247).

P. P. B.

Dimethoxybenzoyl-carbonic Acid and its relation to α-Homoveratric Acid. By FERD. TIEMANN and KAETA AKIMORI MATSMOTO (*Deut. Chem. Ges. Ber.*, xi, 141—145).—Dimethyldioxybenzoyl-carbonic acid (veratroyl-carbonic acid),

$$C_6H_3(OCH_3)_2CO.COOH,$$

is prepared by the oxidation of methyleugenol with a solution of potassium permanganate; the filtrate from the manganese dioxide is acidified and extracted with ether. The residue obtained by evaporation of the ether is dissolved in hot water, from which veratric acid separates on cooling, whilst the veratroyl-carbonic acid remains in solution, and may be obtained by evaporation.

Veratroyl carbonic acid crystallises from anhydrous benzene in white, needle-shaped crystals, but if water be present transparent tabular crystals are formed, which contain water of crystallisation. The dried substance melts at 138—139°. This acid has strongly acid properties; its ammonium and alkaline salts crystallise well; the lead salt has been obtained as a white, difficultly soluble, crystalline precipitate. By further oxidation it yields veratric acid, $C_6H_3(OCH_3)_2.COOH$, and is converted by fusion with potassium hydrate into pyrocatechuic acid, showing that it belongs to the protocatechuic acid series.

α-Homoveratric acid (α-homodimethylprotocatechuic acid),

$$C_6H_3(OCH_3)_2CH_2.COOH.$$

This acid was prepared from α-homovanillic acid by heating 1 mol. of the acid with 2 mols. of KHO, and 2 mols. of CH_3I, and methyl alcohol in sealed tubes, at 140—150°. It crystallises from water in slender, colourless needles, which contain water of crystallisation, and give it up when dried over sulphuric acid in a vacuum; the dehydrated compound melts at 98—99°, dissolves in alcohol and ether, and is less soluble in water than the veratroyl-carbonic acid. It dissolves in concentrated sulphuric acid without coloration, whilst veratroyl-carbonic acid gives a red colour. P. P. B.

Anhydrobenzamidotoluic Acid and a New Ketone Base. By J. T. STODDARD (*Deut. Chem. Ges. Ber.*, xi, 293—297).—The author regards the acid, $C_6H_4.C(NH)(N).C_6H_4.COOH$, obtained by Hahnemann (*Ber.*, xi, 712), by oxidising anhydrotoluene di-amidobenzene, $C_6H_4.C(NH)(N).C_6H_4.CH_3$, as paratoluic acid, in which the three hydrogen-atoms of the methyl group are replaced by

$=$N—C_6H_4—N—, and proposes to name this substance anhydro-ortho-diamidozenzeneparatoluic acid, which may be abbreviated to anhydrobenzamidotoluic acid. This acid is almost insoluble in cold water, but dissolves more readily in alcohol and in hot water. The alcoholic solution deposits needle-shaped crystals, which melt at about 300°, and contain 2 molecules of water of crystallisation. The anhydrotoluenediamidobenzene (m. p. 268°) is most easily prepared by reducing tolueneorthonitranilide from paratoluic chloride, and oxidising the base produced with chromic mixture. The ethyl ether is insoluble in water, but crystallises from alcohol in colourless needles, melting at 242—244°. The barium salt, $(C_{14}H_9N_2O_2)_2Ba + 6H_2O$, and the calcium salt, $(C_{14}H_9N_2O_2)_2Ca + 5H_2O$, form small, needle-shaped crystals. The potassium salt, $C_{14}H_9N_2O_2.K + 7H_2O$, crystallises in needles containing 7 molecules of water; it is very soluble in water, and easily forms supersaturated solutions. The silver salt is almost insoluble in water. When heated, it is decomposed into metallic silver, carbon dioxide, oxygen, and a new base, having the composition $C_{27}H_{18}N_4O$, which it is proposed to call *anhydrotolylketamine*. The free base melts at 277°; it is soluble in alcohol, and unites with hydrochloric acid, forming a hydrochloride, $C_{27}H_{18}N_4O.2HCl + 2H_2O$, soluble in water, but almost insoluble in aqueous hydrochloric acid. It gives a double salt with platinic chloride.

W. C. W.

Products of the Dry Distillation of Calcium Pimarate. By G. BRUYLANTS (*Deut. Chem. Ges. Ber.*, xi, 447—448).—In addition to the fatty hydrocarbons, previously stated by the author to be the sole products of the decomposition of calcium pimarate by heat, he has identified toluene, dimethylbenzene, methylethylbenzene, terebene, and diterebene, *i.e.*, hydrocarbons of the aromatic and camphor groups. The nature of this decomposition, and also that of the sodium salt by heat, and the action of iodine on the free acid, leads the author to regard pimaric acid as resulting from the union of two molecules of the hydrocarbon, $C_{10}H_{16}$, and as having the constitutional formula,

$$(C_3H_7)(CH_3)C_6H_6\text{—}C_6H_6(CH_3)(C_3H_5O).$$

C. F. C.

Isomeric Nitrophthalic Acids. By O. MILLER (*Deut. Chem. Ges. Ber.*, xi, 393).—The addition of water to the crude product of the action of a mixture of nitric and sulphuric acids on phthalic acid throws down two isomeric nitrophthalic acids, together with picric acid. The ordinary prismatic nitrophthalic acid is easily obtained by repeated recrystallisation of this crude product from water, but the more soluble isomeride is difficult to isolate, as it forms a compound with picric acid. It crystallises in yellowish needles, which melt at 160°, and decompose at 165°. It is easily soluble in water, alcohol, and ether, but insoluble in benzene.

The barium salt, $C_6H_3NO_2(COO)_2Ba + 2H_2O$, forms a pale yellow precipitate, composed of microscopic scales. The silver salt,

$$C_6H_3NO_2(COOAg)_2.$$

is slightly soluble in water, but dissolves easily in very dilute ammonia.

W. C. W.

Constitution of Xylenethiamide. By IRA REMSEN (*Deut. Chem. Ges. Ber.*, xi, 465—467).—In this paper the author discusses the bearings of certain of his observations on the validity of Jacobsen's formulæ for the xylene thiamides (m. p. 96° and 137°), viz.:—

$$CH_3 : SO_2.NH_2 : CH_3 = 1 : 2 : 3$$
$$\text{and } CH_3 : CH_3 : SO_2.NH_2 = 1 : 3 : 4$$

(*Ber.*, xi, 17). The author finds that the first-mentioned thiamide yields a monobasic acid, as the sole product of its oxidation by chromic acid, and can scarcely, therefore, be held to have its two methyl-groups symmetrically arranged in relation to the SO_2NH_2 group.

Mesitylenesulphonic acid is similarly oxidised to a monobasic acid. Here, therefore, two methyl groups withstand, whilst the other, most probably the para-group, yields to the oxidising action.

These facts are referable to similar causes, which are under further investigation. C. F. C.

Oxidation of Xylenethiamides. By M. W. ILES and IRA REMSEN (*Deut. Chem. Ges. Ber.*, xi, 462—465).—By fusion with potassium hydrate the authors have converted p-thiaminetoluic acid into the corresponding oxyacid. This acid crystallises from its aqueous solution in tufts of long needles, which melt at 169°, and may be sublimed without decomposition. The calcium and barium salts, $\{C_6H_3.OH.CH_3.COO\}_2R''.3H_2O$, as well as those of silver, copper, and manganese, all of which are crystalline, are described. The oxytoluic acid yields a crystalline nitro-derivative, melting at 86°. Whereas p-thiaminetoluic acid is the sole product of the oxidation of xylenethiamide (m. p. 96°) by chromic acid, this amide is oxidised by potassium permanganate to a bibasic acid, *thiaminisophthalic acid*,

$$C_6H_3.SO_2NH_2.(COOH)_2,$$

which crystallises in long, colourless needles, melting at 283°.

The barium and calcium salts of this acid crystallise readily; the silver salt is amorphous. Thiamineparatoluic acid, when oxidised by permanganate, also yields a bibasic acid, which is probably a thiamineterephthalic acid. C. F. C.

Constituents of Aurin. By ZULKOWSKY (*Deut. Chem. Ges. Ber.*, xi, 391).—The author has obtained the following substances from aurin:—(1.) $C_{19}H_{14}O_3$, which forms large red crystals. (2.) A derivative of (1), $C_{19}H_{16}O_6$, small violet needles, easily decomposed by heat. (3.) $C_{20}H_{16}O_3$, green, needle-shaped crystals, having a metallic lustre. (4.) $C_{20}H_{18}O_3$, the hydro-derivative of the preceding body. (5.) An amorphous resin, colourless in the pure state, which yields on oxidation: (6.) A red amorphous powder, resembling the compound obtained by Baeyer (*Ber.*, ix, 1237) from phthalideïn and phenol.

Dale and Schorlemmer's compound, $C_{20}H_{14}O_3$, could not be found in the specimen of aurin examined. W. C. W.

A Base, $C_{19}H_{18}N_2$. By C. BÖTTINGER (*Deut. Chem. Ges. Ber.*, xi, 276—277).—This base, whose hydrochloride is formed in small quantities by evaporating on a water-bath an ethereal solution of 1 molecule of benzyl chloride and 2 molecules of aniline, is best prepared by warming a mixture of 4 grams of benzyl chloride and 4·65 grams of aniline, until dark bands appear in the liquid. The mixture is then cooled rapidly, a violent reaction taking place. The solidified product is dissolved in alcohol, and the solution evaporated on a water-bath, the residue being treated first with water and then with ammonia. In this way the base is precipitated as a heavy white powder, which is easily soluble in alcohol, ether, and dilute acids, but not in water. The solutions of some of its salts possess fine colours, and exhibit fluorescence.

Its hydrochloride is soluble in alcohol, and its aqueous solutions, when boiled with ferric chloride, give a violet substance. Its sulphate yields a violet mass with potassium bichromate. Bromine acts energetically on the aqueous solution of the base. Sodium amalgam and potassium nitrate have no action on it. It melts at about 67°.

The base is di-acid, and forms a platinochloride $(C_{19}H_{18}N_2)2HCl.PtCl_4$, which is a yellow brown powder, easily soluble in water and warm alcohol. P. P. B.

Action of Benzoyl Chloride on Leucine. By A. DESTREM (*Compt. rend.*, lxxxvi, 484—486).—The author has commenced a series of experiments on the acid amides homologous with glycocine, by the reaction of benzoyl chloride on leucine. On mixing thoroughly dried leucine with the chloride in a flask, and heating at 100°, the mixture fuses and becomes of a yellow colour, whilst long needles of benzoic acid are formed on the surface, the reaction being terminated when the evolution of hydrochloric acid ceases. The mass is then treated with tepid water to remove the benzoic acid, leaving a yellow substance which, when treated with hot alcohol, partly dissolves; the analysis of the insoluble portion leads to the formula, $C_{12}H_{24}N_2O_3$, that of the anhydride of amido-caproic acid (leucine) $C_6H_{12}NO—O—C_6H_{12}NO$, the reaction taking place thus:—

$$2C_6H_{13}NO_2 + C_7H_5O.Cl = C_7H_5O.OH + HCl + C_{12}H_{24}N_2O_3.$$

The body is a white amorphous powder becoming gelatinous after repeated washing with boiling alcohol, and reconverted into leucine with difficulty even after prolonged boiling in water. The author thinks that the partial dehydration of leucine, and its reconversion, may be applied in the synthesis of quaternary organic bodies containing nitrogen. The portion soluble in alcohol had the formula, $C_{26}H_{32}N_2O_5$, or $(C_6H_{11}NO.C_7H_5O)_2O$, that is, the anhydride of amidocaproic acid when two atoms of hydrogen are replaced by twice the radicle benzoyl. It is yellow and amorphous, soluble in alcohol, insoluble in water, melts at 85°, decomposes in boiling water into benzoic acid and the anhydride first mentioned, and on heating on platinum foil is decomposed, giving off benzoic acid. J. M. T.

Action of Ammonia on Isatin. By E. v. SOMMARUGA (*Liebig's Annalen*, cxc, 367—384).—When an alcoholic solution of isatin saturated with dry ammonia gas is heated in sealed tubes at 100° for 24 hours, it forms two crystalline bodies differing in their solubility in water and alcohol, a resinous substance, and a very small quantity of a purplish-violet colouring matter. *Isatindiamide* forms pale yellow crystals, which melt with decomposition at 111°, and are sparingly soluble in alcohol and in water. This substance unites with acids to form salts. The hydrochloride, $C_{16}H_{12}N_4O_2.HCl$, and the nitrate, $C_{16}H_{12}N_4O_2.HNO_3$, are yellow crystalline powders, which are but slightly soluble in water. The existence of these salts is considered by the author to show that the molecule of indigo contains 16 atoms of carbon.

The easily soluble crystalline body has the composition, $C_{16}H_{14}N_6O_3$. It forms large colourless needle-shaped crystals melting between 295° and 300°, which dissolve in dilute acids.

The resinous substance, $C_{16}H_{11}N_3O_2$, after being dissolved in potash and reprecipitated by an acid, forms a yellowish powder resembling tannin in appearance. It melts with decomposition at 209—210°, and is soluble in alcohol and in water.

The formation of the resin and of the soluble crystalline body may be represented thus:—

$$4C_{16}H_{10}N_2O_4 + 7NH_3 = 3C_{16}H_{11}N_3O_2 + C_{16}H_{14}N_6O_3 + 7H_2O.$$

The author finds that Erdmann's process for preparing isatin (*J. pr. Chem.*, xcv, 176) by oxidising indigo with chromic acid yields the best results.

W. C. W.

Dithymoxyl-ethane. By A. STEINER (*Deut. Chem. Ges. Ber.*, xi, 287—289.)—Dithymoxyl-ethane is prepared by adding a mixture of chloroform and tin tetrachloride to a well cooled mixture of thymol (50 pts. by weight) and para-aldehyde (10 pts. by weight). The yellow viscous mass so obtained is freed from thymol by distilling in a current of steam; and by crystallising the solid residue from hot benzene, dithymoxylethane is obtained in the form of small white needles. Crystallised from alcohol, it forms large plates, which effloresce on exposure to the air. It melts at 185°, is easily soluble in cold alcohol, methyl alcohol, ether and chloroform, less easily in cold benzene, and is almost insoluble in boiling petroleum ether. Dithymoxyl-ethane distils without decomposition; it dissolves more easily in hot caustic potash than in cold, and is precipitated from this solution by acids. Jäger has already prepared this compound by the reduction of dithymoxyl-trichlorethane, and finds its melting point to be 180° (this *Journal*, 1877, i, 262).

Diacetyldithymoxyl-ethane, is prepared by heating dithymoxyl-ethane and acetic anhydride at 160—170° for several days. It crystallises from alcohol in small colourless needles, melting at 100°, and may be distilled without decomposition. It dissolves easily in cold alcohol, ether, acetone, chloroform and benzene, also in hot petroleum ether, but is insoluble in water.

Dibenzoyldithymoxyl-ethane is prepared by heating dithymoxyl-ethane and benzoyl chloride for several hours at 150°. It crystallises from boiling alcohol in colourless needles, which melt at 191°. It is easily soluble in chloroform, in hot alcohol, ether and acetone, less easily in cold. It distils without decomposition.

Diethyldithymoxyl-ethane is formed by heating on a water-bath an alcoholic solution of dithymoxyl-ethane with the calculated quantities of ethyl iodide and potassium hydrate in a flask connected with a reversed condenser. It crystallises from alcohol in tufts of needles which melt at 72°; at 100° these crystals give up the alcohol of crystallisation they contain, and form a viscous mass which solidifies finally to a porcelain-like mass. The ether is insoluble in water, easily soluble, however, in alcohol, ether, chloroform, acetone, petroleum-ether, and methyl alcohol.

Dithymoxyl-ethane and the diacetyl-compound yield thymoquinone when oxidised by a mixture of manganese dioxide and sulphuric acid.

P. P. B.

A Trinitronaphthol. By A. G. ECKSTRAND (*Deut. Chem. Ges. Ber.*, xi, 161—163).—A trinitronaphthol (naphthopicric acid), $C_{10}H_4(NO_2)_3OH$, is formed on heating dinitronaphthol with four times its weight of a mixture of fuming and ordinary strong nitric acids. The product is freed from unaltered dinitro-compound repeated by crystallisation from glacial acetic acid, till the crystals melt constantly at 176°.

Trinitronaphthol crystallises in small bright-yellow laminæ or prisms, which are slightly soluble in alcohol, benzene, and boiling water. It forms crystallisable salts, of which the following have been examined.

Potassium salt, $C_{10}H_4(NO_2)_3OK + H_2O$. Fine red laminæ or needles, soluble in 397 parts of cold water. *Sodium salt*, $C_{10}H_4(NO_2)_3ONa + H_2O$. Red prismatic crystals, soluble in 35 parts of cold water. The *ammonium salt* crystallises in long orange-coloured needles soluble in 633 parts of cold water. *Barium salt*, $[C_{10}H_4(NO_2)_3O]_2Ba + 2\frac{1}{2}H_2O$: yellow needles, which turn red on heating, and dissolve in 1106 parts of cold water. *Calcium salt*, $[C_{10}O_4(NO_2)_3O]_2Ca + 3\frac{1}{2}H_2O$: yellow needles, soluble in 265 parts of cold water. The *lead* and *silver salts* also crystallise in yellow needles.

All the salts are soluble in alcohol. They explode when heated.

Trinitronaphthol is reduced by tin and hydrochloric acid to *triamidonaphthol*, which combines with stannous chloride to form the crystalline compound, $C_{10}H_4(OH)(NH_2)_3.HCl + SnCl_2 + H_2O$.

J. R.

Compounds of Naphthalene with Chloral. By J. GRABOWSKI (*Deut. Chem. Ges. Ber.*, xi, 298—303).—*α*- and *β-dinaphthyl-trichlorethane*, $CCl_3.CH(C_{10}H_7)_2$, are prepared by gradually mixing 8 parts of naphthalene, 3 of chloral, and 6 of chloroform, with 6 parts of sulphuric acid, and then adding 6 parts of fuming sulphuric acid. When the mixture, which should be kept cool, assumes a bluish-violet colour, it is diluted with about 20 parts of water, and the chloroform distilled off. The residue is washed with water, and treated with alcohol, leaving an insoluble residue of *β-dinaphthyl-trichlorethane*, whilst the filtrate contains *α-dinaphthyl-trichlorethane*, which, however, has not been obtained in the pure state. The alcoholic solution is used for preparing α-dinaphthyl-trichlorethene.

The β-compound is soluble in benzene, chloroform and aniline, and is deposited from its solution in benzene in diclinic crystals melting at 156°. When boiled with alcoholic potash or distilled, it loses hydrochloric acid, and is transformed into β-dinaphthyl-dichlorethylene, whilst with zinc-dust it yields a mixture of β-dinaphthyl-dichlorethene, naphthalene, dinaphthyl-acetylene, and dinaphthyl-anthrylene.

α-Dinaphthyl-dichlorethylene, $C_{22}H_{14}Cl_2$, is obtained by distilling with lime the residue left on evaporating the alcoholic solution mentioned above. The distillate dissolved in a very small quantity of hot benzene, deposits almost all the β-dinaphthyl-dichlorethylene when left at rest, and the mother-liquor contains the α-compound. This substance forms colourless silky crystals, melting at 150°, which are soluble in hot alcohol, but much more readily in ether, benzene, and chloroform. The α-derivatives are less stable than the corresponding β-compound.

β-Dinaphthyl-dichlorethylene, prepared by distilling crude trinaphthyl-trichlorethane, or by heating it at 180° for 24 hours, forms short prismatic crystals, which melt at 219°, and boil above 360°. It is soluble in ether, chloroform, benzene and fused naphthalene. It yields a bromo- and a tetranitro-derivative.

Tetranitro-β-dinaphthyl-trichlorethane, $C_{22}H_{11}N_4O_8Cl_3$, produced by the action of fuming nitric acid on β-dinaphthyl-trichlorethane, is a yellowish crystalline powder, which melts at 258°, and is insoluble in the usual solvents.

Tetranitro-α-dinaphthyl-dichlorethylene, $C_{22}H_{10}N_4O_3Cl_2$, melts at 213—214°, the corresponding β-compound melts at 292—293°.

Dinaphthyl-acetylene, $C_{22}H_{14}$ or $C_{10}H_7.C{\equiv}C.C_{10}H_7$, is obtained by heating dinaphthyltrichlorethane with soda-lime, in a combustion tube. The resinous distillate, after rectification, is treated with ether; the ethereal solution on evaporation yields needle-shaped crystals of dinaphthyl-acetylene, which melt at 225°, and boil above 360°. It yields a nitro-derivative.

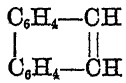
Dinaphthyl-anthrylene appears to be formed under the same conditions as the preceding hydrocarbon, and always accompanies it. It is best prepared, however, by heating a mixture of β-dinaphthyl-trichlorethane and zinc oxide to redness in a combustion tube. The distillate is boiled with ether and filtered, the residue dissolved in benzene deposits large violet-coloured scales of dinaphthylanthrylene. This substance forms a crystalline compound with picric acid, which may be taken advantage of for its purification. It melts at 270°, and sublimes readily. Dinaphthyl-anthrylene, $C_{22}H_{12}$, bears the same relation to dinaphthylacetylene that phenanthrene does to stilbene—

$C_6H_5—CH{=}CH—C_6H_5$

Stilbene.

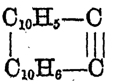
$C_{10}H_7—C{\equiv}C—C_{10}H_7$

Dinaphthyl-acetylene.



$$\begin{array}{l} C_6H_4—CH \\ |\qquad\;\; \| \\ C_6H_4—CH \end{array}$$

Phenanthrene.



$$\begin{array}{l} C_{10}H_5—C \\ |\qquad\;\; ||| \\ C_{10}H_6—C \end{array}$$

Dinaphthyl-anthrylene.

W. C. W.

Comparison of ε-Purpurin with Purpuroxanthincarbonic Acid, and on Anthraflavone. By E. SCHUNCK and H. RÖMER (*Deut. Chem. Ges. Ber.*, xi, 431—434).—A reply to the strictures of Rosenstiehl (*Ber.*, x, 2166). C. F. C.

Chlorine- and Bromine-Derivatives of Phenanthrene. By G. ZETTER (*Deut. Chem. Ges. Ber.*, xi, 164—173).—A solution of phenanthrene in glacial acetic acid absorbs chlorine readily in the cold, and gives off hydrogen chloride. The product of the reaction consists mainly of dichlorophenanthrene tetrachloride, but contains also dichloro- and monochloro-phenanthrene.

Dichlorophenanthrene tetrachloride, $C_{14}H_8Cl_2.Cl_4$, crystallises in small colourless needles, which dissolve very easily in alcohol, ether, benzene, and toluene, melt at 145°, and give off hydrogen chloride at a slightly higher temperature. When heated with alcoholic potash, it loses first one and then a second atom of chlorine, yielding tetrachlorophenanthrene.

Dichlorophenanthrene, $C_{14}H_8Cl_2$, is an amorphous white substance, easily soluble in glacial acetic acid, ethyl acetate, alcohol, ether, benzene, and toluene. It melts to a transparent oily liquid at a low temperature.

Monochlorophenanthrene, $C_{14}H_9Cl$, is an oily liquid, easily soluble in the liquids named above, but not in water. It carbonises when slightly heated.

Tetrachlorophenanthrene, $C_{14}H_6Cl_4$, is formed by the action of antimony pentachloride on phenanthrene in the cold, or by the action of iodine chloride at 100—110°. It crystallises in small yellowish needles, which dissolve easily in ether, benzene, and toluene, but very slightly in alcohol. The crystals melt at 171—172°, and sublime in thin yellowish needles. Neither this nor any of the higher chlorinated products is affected by boiling with alcoholic potash.

Hexchlorophenanthrene, $C_{14}H_4Cl_6$, is formed by the action of antimony pentachloride on phenanthrene in closed tubes at 120—140°, or in the oil-bath at 180—200°. It sublimes in white feathery crystals, which melt at 249—250°, and dissolves very sparingly in alcohol, ether, and acetic acid.

Octochlorophenanthrene, $C_{14}H_2Cl_8$, is produced on heating phenanthrene with excess of antimony pentachloride at 180—200°. It crystallises in indistinct granular forms, and sublimes in yellow needles, which melt at 270—280°. It is nearly insoluble in alcohol and ether, but dissolves easily in benzene and toluene.

Dibromophenanthrene, $C_{14}H_8Br_2$, is formed by the action of bromine on phenanthrene in ethereal solution. It crystallises from alcohol in long needles, melts at 148°, and sublimes in yellow needles. Most solvents dissolve it readily, and deposit it in crystals when evaporated.

A compound isomeric with the preceding, and formed together with it, crystallises in tables which melt at 158°, and do not sublime even when strongly heated. It dissolves easily in the ordinary solvents, and crystallises from the solutions on evaporation.

Neither of these dibromo-compounds is attacked by boiling alcoholic potash.

Tribromophenanthrene, $C_{14}H_7Br_3$, is formed by heating phenanthrene at 130—140°, with the calculated quantity of bromine. The purified product melts at 125—126°, and has all the properties of Hayduk's tribromophenanthrene (*Annalen*, clxvii, 177).

Tetrabromophenanthrene, $C_{14}H_6Br_4$, is produced when phenanthrene is heated at 200—210° with the requisite quantity of bromine. It forms small granular crystals, which melt at 183—185°, and dissolve in benzene and toluene, but scarcely in alcohol or ether.

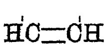
Hexbromophenanthrene, $C_{14}H_4Br_6$, is formed on heating phenanthrene at 280° with the calculated quantity of bromine and 1 mol. of iodine. It sublimes in snow-white needles, which melt at 245°, and dissolve in glacial acetic acid, benzene, and toluene.

Heptabromophenanthrene, $C_{14}H_3Br_7$, is produced by heating phenanthrene with excess of bromine containing iodine at 300°, or above, in sealed tubes. It sublimes in small yellowish needles which melt above 270°. J. R.

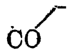
Oxidation of Phenanthrene-quinone by Potassium Permanganate. By R. Anschütz and F. R. Japp (*Deut. Chem. Ges. Ber.*, xi, 211—215).—Pure phenanthrene-quinone, when treated with very weak soda-ley and potassium permanganate at 100° yields diphenylene-ketone. When boiled with weak soda-ley alone, it yields diphenylene-glycollic acid, and when heated with dilute solution of permanganate alone it yields diphenic acid.

Diphenylene-ketone and diphenic acid, when further oxidised with alkaline permanganate, yield phthalic acid, but apparently no isophthalic or terephthalic acid. The same product was obtained also by the oxidation of sodium phenanthrene-sulphonate with potassium permanganate.

The authors conclude from these results that phenanthrene and diphenylene-ketone are diortho-compounds, as supposed by Fittig and Ostermeyer (*Liebig's Annalen*, clxvi, 380; see also *Ber.*, x, 2144), and may therefore be represented by the formulæ—



Phenanthrene.



Diphenylene-ketone.

J. R.

Constitution of Phenanthrene. By G. Schultz (*Deut. Chem. Ges. Ber.*, xi, 215—218).—Griess's diamido-diphenic acid,

$$C_{12}H_6(NH_2)_2(COOH)_2,$$

is converted by treatment with nitrous acid, in presence of nitric or hydrochloric acid, into tetrazo-diphenic acid, and this, when boiled with hydriodic acid yields di-iodo-diphenic acid, $C_{12}H_6I_2(COOH)_2$, a yellow body dissolving easily in alcohol and melting about 260°. Di-iodo-diphenic acid is converted by the action of sodium-amalgam into diphenic acid, $C_{12}H_8(COOH)_2$, identical with that obtained from phenanthrene.

Now, since in Griess's diamido-acid the two groups COOH occupy ortho-positions in the benzene-nuclei, it follows from the foregoing series of reactions that phenanthrene is also a diortho-compound (see the preceding paper). J. R.

Proximate Composition of certain Volatile Oils. By G. BRUYLANTS (*Deut. Chem. Ges. Ber.*, xi, 449—456).—*Oil of Tansy.*—By the addition of a concentrated solution of $NaHSO_3$ and alcohol to the oil, a crystalline compound is obtained, from which the aldehyde $C_{10}H_{16}O$ may be isolated. It is a liquid boiling at 195°, of sp. gr. 0·918 (at 4°), and is isomeric with laurel camphor. The filtrate from the above compound yields by fractional distillation a terpene, $C_{10}H_{16}$ (b. p. 155—160°), and an alcohol, $C_{10}H_{18}O$ (b. p. 203—205°). Tansy oil contains these bodies in the following approximate ratios :—

Terpene,	$C_{10}H_{16}$	1 per cent.
Aldehyde,	$C_{10}H_{16}O$ ..	70 „
Alcohol,	$C_{10}H_{18}O$ ..	26 „

Valerian oil appears from the author's investigation to be composed of the following proximate constituents: terpene, $C_{10}H_{16}$; the alcohol, $C_{10}H_{18}O$; together with its formic, acetic, and valeric ethereal salts, and the ether $(C_{10}H_{17})_2O$. The compound $C_{10}H_{18}O$, isomeric with borneol, when acted on by phosphoric anhydride, yields the terpene $C_{10}H_{16}$, whilst with chromic mixture it is oxidised, with formation of camphor, $C_{10}H_{16}O$, together with formic, acetic, and valeric acids. C. F. C.

Borneo Camphor. By J. KACHLER (*Deut. Chem. Ges. Ber.*, xi, 460).—This is a preliminary communication of the results of a comparative investigation of Borneo camphor of natural occurrence (*Dryobalanops*), and that obtained by Baubigny's method from laurel camphor. Both bodies are found by the author to yield the same chloride, $C_{10}H_{17}Cl$ (m. p. 147°), on treatment with phosphorus pentachloride or concentrated hydrochloric acid. This chloride is easily resolved, by heating in sealed tubes with water at 100°, into hydrochloric acid and a solid camphene, $C_{10}H_{16}$ (m. p. 51°), which appears to be identical with that prepared by Spitzer (*Ber.*, x, 1034).

C. F. C.

Compounds of the Camphor Group. By J. KACHLER (*Liebig's Annalen*, cxci, 143—173).—*Oxidation-products of Camphor.*—In oxidising camphor by means of nitric acid, the author found (*Ber.*, iv, 381), that the mother-liquors from the camphoric acid formed contain a new acid, camphoronic acid. A further examination of larger quantities of these mother-liquors has shown that several other acids are produced. After the greater portion of the camphoric acid has been separated from the mother-liquors, they are heated in a porcelain basin until red fumes cease to be given off, whereby a reddish-yellow, transparent, turpentine-like mass is obtained, which on standing for three to six months becomes crystalline. From this mass by fractional crystallisation, &c., the following acids have been obtained :—Camphoric acid, $C_{10}H_{16}O_4$; mesocamphoric acid, $C_{10}H_{16}O_4$; camphoronic acid, $C_9H_{12}O_5$; hydro-oxycamphoronic acid, $C_9H_{14}O_6$; acid (A),

$C_9H_{12}O_7$; acid (B), $C_7H_{12}O_5$ (?); dinitro-heptylic acid, $C_6H_{10}N_2O_6$; acid (D) (?). From 5 kilos. of camphor the following quantities of the above were obtained:—1·7 kilos. of camphoric acid, 1·8 kilos. of crude camphoric acid as turpentine-like mass, from which were separated 0·1 kilo. of dinitroheptylic acid, and 0·2 kilo. of acids (A, B, C, and D). A large quantity of camphor is lost in the oxidation. The gases formed consisted chiefly of carbonic acid and small quantities of hydrocyanic acid. Mesocamphoric acid, $C_{10}H_{16}O_4$, is isomeric with camphoric acid, melts at 120°, and solidifies to a transparent glass. This acid has been described by von Wreden (*Annalen*, cxxix, 327), who obtained it by the action of hydriodic acid on camphoric acid; it is also formed when camphoric acid is heated with water (Jungfleisch, *Ber.*, vi, 268), and by the action of concentrated sulphuric acid on camphoric acid (Kachler, *Annalen*, cxxix, 179). This acid is soluble in cold water, melts to an oil in hot water, and crystallises in fine needles.

Hydro-oxycamphoric acid, ($C_9H_{14}O_6$), separates from water in beautiful crystals which belong to the triclinic system. It is soluble in cold water, and very easily soluble in hot water; it melts at 164·5°. Its aqueous solutions have a strongly acid reaction, and give no precipitate with ammonia and barium chloride, in which it differs from camphoric acid.

Three of the hydrogen atoms in hydro-oxycamphoric acid can be replaced by metals, and it also forms mono- and bi-basic-acid salts. The *acid ammonium salt*, $C_9H_{13}(NH_4)O_6$, crystallises in colourless needles, forming globular aggregations, and melts at 178°, solidifying after some time to a porcelain-like mass. The neutral ammonium and potassium salts crystallise well, and deliquesce on exposure to the air.

The *acid calcium salt*, $C_9H_{12}CaO_6 + 2H_2O$, is easily soluble in water, and crystallises in silky needles concentrically grouped. The corresponding *barium salt* has only been obtained as a gummy mass.

The *neutral calcium salt*, $C_9H_{11}Ca'_3O_6$ ($Ca' = 20$), has been obtained as a colourless gummy mass. The corresponding *barium salt*, $C_9H_{11}Ba'_3O_6$ ($Ba' = 68·5$), separates as crystalline scales, which are easily soluble in water.

The *neutral copper salt*, $C_9H_{11}Cu'_3O_6$ ($Ca = 31·7$), is obtained as a bluish-green precipitate by boiling the aqueous solution of the acid with copper acetate. When dried it forms a bluish-green powder insoluble in water.

The *neutral silver salt*, $C_9H_{11}Ag_3O_6$, is a white precipitate almost insoluble in cold water, but soluble in hot.

Hydro-oxycamphoronic acid heated with bromine in sealed tubes at 120—125°, gives hydrobromic acid and an acid melting at 226°, having the composition $C_9H_{12}O_6$, and therefore isomeric with oxycamphoric acid.

Dinitroheptylic acid, $C_6H_{10}N_2O_6$, crystallises from hot water in shining plates, resembling in appearance boric acid. It is soluble in alcohol, ether, and chloroform, and melts at 215°. From alcohol it crystallises in well-developed crystals, which, according to the determinations of von Zepharovich, are monoclinic. This acid has already been prepared by Kullhem (*Annalen*, clxiii, 231), by boiling the mother-liquors of camphoric acid with nitric acid. By carefully heating this acid in small quantities it may be distilled; if heated quickly it takes fire, detonating slightly. The aqueous solution of the ammonium salt gives with copper acetate a bluish precipitate, soluble in excess of the precipitant. The aqueous solution of the acid is not precipitated by copper acetate or lead acetate solution; solutions of the neutral salts, however, form with the latter a white flocculent precipitate, which is soluble in large quantities of hot water, crystallising from this solution in the form of hexagonal plates.

Kullhem has described the barium salt as containing $2\frac{1}{2}$ mols. of water of crystallisation. The author has obtained a barium salt having the composition $C_6H_9Ba'N_2O_6 + 1\frac{1}{2}H_2O$. This salt was obtained by boiling the acid with baryta-water, removing the excess of baryta by means of carbonic acid, and allowing the solution to evaporate over sulphuric acid. It crystallises in long concentric needles.

Action of Sodium-amalgam on Dinitroheptylic Acid.—In repeating the experiments of Kullhem (*Annalen*, clxvii, 45), of the action of sodium amalgam on an alcoholic solution of this acid, the author finds, as did Kullhem, that mononitroheptylic acid and ammonia are formed, the action taking place as follows:—

$$C_6H_{10}N_2O_6 + 4H_2 = C_6H_{11}NO_4 + NH_3 + 2H_2O.$$

A small portion of the dinitro-acid is, however, so acted upon as to produce CO_2 and nitrous acid; the formation of this latter accounts for the fact that the mononitro-acid when liberated from the sodium salts assumes a bluish-green colour.

Mononitroheptylic acid is obtained in beautiful transparent crystals by evaporating its aqueous solution over sulphuric acid. These crystals are, according to von Zepharovich, monoclinic. It volatilises below 100°, and the author finds that by melting it repeatedly, its melting point may be lowered from 116° to 111·5°; it may be distilled without decomposition. Kullhem has investigated several of the salts of mononitroheptylic acid, to which he attributes the general formula $C_6H_{10}M'NO_4$. Mononitroheptylic acid treated with nitrous acid gives rise to a blue coloration, thus resembling the "pseudonitrols" of Meyer (*Annalen*, 175·88), which contain the group $\equiv CH.NO_2$, and which should render two atoms of hydrogen in the mononitroheptylic acid capable of being replaced by metals. This the author finds to be the case, since on boiling the mononitro-acid with baryta-water, a heavy white powder separates out, consisting of slender shining needles having the composition $C_6H_9Ba''NO_4$.

Sodium amalgam acts on aqueous solutions of dinitroheptylic acid so as to produce a small quantity of bromonitroheptylic acid, whilst the larger portion is decomposed to form carbonic acid, nitrous acid, and an oil containing no nitrogen.

Tin and hydrochloric acid act violently upon dinitroheptylic acid, producing a ketone, ammonia, hydroxylamine, and carbonic acid. This ketone boils at 94·1° (cor.), gives the iodoform reaction with iodine and potassium hydrate, and forms a crystalline compound with sodium hydrogen sulphite. Its composition is $C_5H_{10}O$; its properties and products of oxidation show it to be methyl-isopropyl ketone,

$(CH_3)_2CH.CO.CH_3$. Zinc and sulphuric acid act similarly to tin and hydrochloric acid, but more slowly; whilst in alkaline solution, zinc acts in the same manner as sodium amalgam. The action of tin and hydrochloric acid may be expressed as follows:—

$$C_6H_{10}N_2O_6 + 10H = C_5H_{10}O + NH_3 + NH_3O + CO_2 + 2H_2O.$$

The action of potassium hydrate on dinitroheptylic acid in sealed tubes heated to 90° is similar to the action of nascent hydrogen; mononitroheptylic acid, methylisopropyl ketone, and carbonic acid are produced, but in this case the nitrogen is liberated as nitrous acid. Dinitroheptylic acid heated in sealed tubes at 90° with caustic baryta, is partly decomposed, so as to form methylisopropyl ketone, nitrous acid, and carbonic acid, according to the equation—

$$C_6H_{10}N_2O_6 + 2Ba(HO)_2 = C_5H_{10}O + Ba(NO_2)_2 + BaCO_3 + 2H_2O,$$

and another portion yields mononitroheptylic acid.

Bromine, even when heated in sealed tubes at 150°, appears to have no action on dinitroheptylic acid.

Mononitroheptylic acid when treated with tin and hydrochloric acid yields methylisopropyl ketone, carbonic acid, and hydroxylamine, as shown in the following equation:—

$$C_6H_{11}NO_4 + H_2 = C_5H_{10}O + CO_2 + NH_3O.$$

When heated to 90—95° in sealed tubes with baryta-water, the mononitroheptylic acid forms chiefly a basic salt, whilst a portion yields carbonic acid, nitrous acid, and what appears to be methylisopropyl carbinol, as shown by the following equation:—

$$2C_6H_{11}NO_4 + 3Ba(HO)_2 = 2C_5H_{12}O + Ba(NO_2)_2 + 2BaCO_3 + 2H_2O.$$

From the characters of both the mono- and dinitroheptylic acids, the nitrogen atom appears to be attached to that atom of carbon which forms the CO group in the ketone. The ease with which both lose the carboxyl-group shows, with some probability, that it is attached to the carbon atom which itself is attached to three other carbon atoms. The following are probably the structural formulæ of these acids:—

$(CH_3)_2C.(COOH)_2C(NO_2).CH_3$, mononitro-acid.
$(CH_3)_2C.(COOH)_2C(NO_2)_2.CH_3$, dinitro-acid.

How the two nitrogen atoms are arranged in the dinitro acid does not appear; when the compound is acted upon by nascent hydrogen, one part separates as ammonia and another portion as hydroxylamine.

By the use of Meyer's nitroso-compounds the author hopes to prepare these acids synthetically. P. P. B.

Catechins from Gambir. By A. GAUTIER (*Compt. rend.*, lxxxvi, 668—671).—The author has isolated from the dried extract of the *Uncaria Gamba*, *i.e.*, from commercial gambir, three catechins, the composition and properties of which may be conveniently tabulated as follows:—

Catechin.	Composition.		Melting point.	Cryst. form.	Solubility. Pts. sol. in 100 H_2O at 50°.
	Air dried.	Anhydrous.			
A	${}_{40}CH_{38}O_{16}.2H_2O$	$C_{40}H_{38}O_{16}$	204—205°	Oblique prisms	9·9
B	$C_{42}H_{38}O_{16}.H_2O$	$C_{42}H_{38}O_{16}$	176—177°	Microscopic needles.	—
C	$C_{40}H_{38}O_{16}.H_2O$	$C_{40}H_{38}O_{16}$	163°	Microscopic needles.	5·3

The author regards the catechins as constituting a natural class of bodies, isomeric or isologous with one another, presenting the characteristics of unsaturated phenols. C. F. C.

A New Reaction of Chlorophyll. By R. SACHSSE (*Chem. Centr.*, 1878, 121—125).—By the action of sodium on a solution of chlorophyll in benzene, a dark green substance is formed, which dissolves in water, producing an intense emerald-green solution, with a feeble but distinct red fluorescence. The absorption spectrum of this solution is closely related to that of unaltered chlorophyll, although it differs from it in some respects. The sodium compound precipitates salts of copper, lead, barium, and calcium from their solutions; it is decomposed by hydrochloric acid, forming a dark-brown precipitate, soluble in alcohol, and a glucoside, which remains in solution. By boiling with hydrochloric acid, the glucoside yields a substance which answers to many of the tests for dextrose.

The reduction of chlorophyll to dextrose would support the author's views that chlorophyll is one of the first products of assimilation in plants, and that starch and sugar result from the decomposition of the chlorophyll. W. C. W.

Veratrine. By E. SCHMIDT (*Arch. Pharm.* [3], x, 511—532.)—This alkaloïd has been carefully examined by Merk (*Ann. Chem. Phys.*, xcv, 200), who ascribed it to the formula, $C_{32}H_{52}N_2O_8$, and by Weigelin (*Jahbr. f. Fortschr. Pharm.*, 1871, 28), who assigned to it the very different formula, $C_{52}H_{86}N_2O_{15}$. It has been, therefore, re-examined by Schmidt, who obtained 56 grams from 5 kilos. of the seed of the *Veratrum Sabadilla*, by exhausting them with very dilute sulphuric acid, and precipitating the crude base from the concentrated solution by ammonia. It was purified by dissolving it in ether, and repeated precipitation from its solution in hydrochloric acid by ammonia. Crude or commercial veratrine appears to contain three modifications—namely, a crystalline base insoluble in water, an amorphous resinous base, also insoluble in water and an amorphous base which is soluble in water. Schimdt thinks this last is formed from the second during the process of separation. The commercial veratrine is soluble in ether and alcohol, but nearly insoluble in water, and melts at 155°. The crystalline modification appears to be the principal constituent, or to be veratrine proper.

Veratrine crystallises from dilute alcohol in compact groups of short needles, which are readily soluble in alcohol and insoluble in water. They melt at 205°, or considerably higher than commercial veratrine. From nine analyses, Schmidt deduces the formula, $C_{32}H_{50}NO_9$, and he points out that this formula agrees with the analytical numbers obtained by Weigelin and Merk, with the exception of the single determination of the amount of nitrogen which the latter made. The *sulphate*, $(C_{32}H_{50}NO_9)_2.H_2SO_4$, forms an amorphous mass, readily soluble in water, and the *hydrochloride*, $C_{32}H_{50}NO_9.HCl$, is a very similar body; neither of them is crystalline, as stated by Couerbe (*Ann. du Chem.*, 9, 112). The double *gold* salt, $C_{13}H_{50}NO_9.HCl + AuCl_3$, consists of a bulky yellow precipitate, soluble in hot alcohol. The *platinochloride* $2(C_{32}H_{50}NO_9.HCl).PtCl_4$, is a similar bulky amorphous yellow precipitate, easily soluble in alcohol, less soluble in water, and insoluble in ether. The *mercuric* compound, $C_{32}H_{50}NO_9.HCl + HgCl_2$, is a white crystalline precipitate, soluble with comparative facility in water, readily soluble in alcohol, but insoluble in ether.

The two other modifications of veratrine appear from the results of the analysis to have the same formula as that of crystalline veratrine, and their platinum salts are of similar character and constitution. All these are, therefore, isomeric, but their difference in constitution has not yet been ascertained. E. N.

Curarine. By T. SACHS (*Liebig's Annalen*, cxci, 254—260).—According to the author's investigations, curare is soluble to the extent of 75 per cent. in cold water. The curarine contained in it is in combination with sulphuric acid, not with acetic acid, as stated by Roulin and Boussingault. The formula of curarine, as deduced from analysis of the picrate, is $C_{18}H_{35}N$. Curarine hydrochloride and sulphate are both very unstable, and not crystallisable. Solution of curarine acetate gives with *sodium chloroplatinate* a bulky yellowish-white precipitate of the formula, $2(C_{18}H_{35}N,HCl) + PtCl_4$, which speedily decomposes, assuming a violet colour. The acetate gives precipitates also with *potassium and mercury iodide*, *potassium and cadmium iodide*, *potassium cyanoplatinite*, *potassium chloroplatinite*, *gold chloride*, *tannin*, *picric acid*, *potassium and mercury chloride*, *sodium phosphate*, *sodium arsenate*, *potassium iodate*, *potassium thiocyanate*, and *potassium ferrocyanide* and *ferricyanide*.

Preyer's statements with regard to curarine (*Zeitschr. f. Chem.*, viii, 381) are, to a great extent, erroneous. A specimen of Preyer's "curarine sulphate," examined by the author, was found to consist mainly of calcium phosphate and carbonate. J. R.

Pyroxanthin. By H. B. HILL (*Deut. Chem. Ges. Ber.*, xi, 456—460).—The author has investigated the action of bromine upon this body. When both are previously diluted with carbon bisulphide, the reaction proceeds slowly with formation of *dibromopyroxanthin tetrabromide*, $C_{15}H_{10}Br_2O_3.Br_4$. This crystallises from its solution in benzene in small white needles (triclinic). When boiled with absolute alcohol and metallic antimony, it is converted into *dibromopyroxanthin*, $C_{15}H_{10}Br_2O_3$, which crystallises from its solution in alcohol in bright yellow, well-formed needles (monoclinic). It could not be obtained by the direct action of bromine on pyroxanthin. Pyroxanthin yielded no definite products when treated with bromine in presence of water. When pyroxanthin is boiled with zinc-dust and acetic acid to which a little alcohol has been added, hydropyroxanthin is produced.

C. F. C.

On the Constituents of Ergot. By DRAGENDORFF (*Chem. Centr.*, 1878, 125—127, and 141—142).—Ergot contains cellulose, mycose, mannite, oil, cholesterin, ecboline, ergotine, ergotinine, picrosclerotine, methyl- and trimethylamine, leucine, lactic, phosphoric, sclerotic, fuscosclerotic, and scleromucic acids, sclerojodin, scleroxanthin, sclererythrin, and sclerocrystallin. Fresh ergot contains about 30 per cent. of fat, and from 0·64 to 0·79 per cent. of scleromucine and 5·89—6·56 per cent. of sclerotic acid; but after it has been kept for some months, the ergot contains only 20 per cent. of fat and 3 per cent. sclerotic acid, the amount of scleromucin increasing to 3 per cent.

Fuscosclerotic Acid, $C_{14}H_{24}O_7$.—Fuscosclerotic acid and scelerythrin are extracted by ether from ergot which has been previously treated with tartaric acid. The two substances are separated by means of the insolubility of the calcium compound of sclererythrin in ether. When the yellow ethereal solution of fuscosclerotic acid is shaken up with ammonia, the acid passes into the ammoniacal solution, and leaves the ether colourless. Potassium, sodium, and ammonium fuscosclerotates are soluble in water.

Picrosclerotin is less soluble in ether than fuscosclerotic acid. It is difficultly soluble in pure water, but dissolves easily in very dilute acids, and is reprecipitated by ammonia. Picrosclerotin contains nitrogen, has a bitter taste, and is a very active poison.

W. C. W.

Preparation of Blood Crystals. By R. GSCHEIDLEN (*Pflüger's Archiv. f. Physiol.*, xvi, 421—426).—If defibrinated blood be sealed up along with air, and kept in a hot oven for some time, and if a little be then diluted with water, placed on a glass slide, and covered with glass, large crystals soon begin to appear. Crystals 3·5 c.m. in length were thus obtained from dog's blood. The author's experiments appear to show that large crystals are thus obtained because the preliminary treatment, by a process of fermentation, removes certain substances, which, under ordinary circumstances, interfere with the growth of the crystals. M. M. P. M.

Proteïn Substance from Bertolletia (Para-) Nuts. By H. RITTHAUSEN (*Pflüger's Archiv. f. Physiol.*, xvi, 301—308).—Chiefly controversial. From his own analysis, and from those of Weyl (who objects to the assertion of the author that these nuts contain a definite proteïn-compound), it is shown that the substance obtained by the action of dilute potash on the powdered kernels previously freed from fatty matter, is of definite composition. M. M. P. M.

Physiological Chemistry.

Production of Heat in Warm-blooded Animals. By D. FINKLER (*Pflüger's Archiv. f. Physiol.*, xv, 603—633).—These experiments confirm the important results formerly obtained by Colasanti. (This *Journal*, 1877, i, 527.) F. J. L.

On the Amount of Disodic Orthophosphate in the Serum of Herbivora. By MRATSCHKOWSKY (*Deut. Chem. Ges. Ber.*, xi, 420).—Phosphates are present in the serum of calves and sheep in too small quantities to permit of their exercising an important influence on the absorption of carbon dioxide by the serum. W. C. W.

On the Constituents of Blood-Serum, by which the Absorption of Carbon Dioxide is Determined. By SETSCHENOFF (*Deut. Chem. Ges. Ber.*, xi, 417—420).—Sertoli considers that that portion of the potash, soda, magnesia, and lime in the serum of oxen, horses, dogs, swine, and men, which is not combined with inorganic acids, exists in combination with albumin. In proof of the acid properties of albumin, he describes an experiment showing the decomposition of sodium bicarbonate by albumin in a vacuum. Setschenoff denies that the decomposition of sodium bicarbonate in a vacuum is influenced by the presence of albumin. He considers that the absorption of carbon dioxide by the serum is due not to the albuminoïds, but to the fats. A portion of the sodium carbonate is converted into neutral carbonate; this saponifies a portion of the fat. When carbon dioxide is absorbed, it not only combines with the carbonates, but also acts on the salt of the fatty acid. W. C. W.

Transudation and Diffusion through the Walls of the Capillary Vessels. By H. NASSE (*Pflüger's Archiv. f. Physiol.*, xvi, 604—634).—The author's experiments relate to diffusion between blood-corpuscles and serum, in presence of water and common salt, and to the influence exerted by carbon dioxide and by oxygen on the exchange of water and salt.

In the first series of experiments horse's blood was used, when it was found that a certain proportion, varying from 13·2 to 19·8 per cent. of the water added, penetrates into the blood corpuscles, the amount so penetrating increasing in a ratio somewhat greater than that of the total amount of water added. In different bloods, equally diluted, the total amount of water given up by the serum to the clot increases with the increase in the amount of clot present. On adding water the blood-corpuscles give up common salt (and probably other salts also), the amount increasing with the proportion of water penetrating these corpuscles; but the quantity of salt so passing from the corpuscles is small relatively to the amount of water absorbed. Horse's blood was also used for the second set of experiments, in which common salt dissolved in serum, was added to the blood. The results showed that an increase in the amount of common salt in blood causes a diminution in the water of the blood-corpuscles, the amount of the change with the same blood being dependent on the amount of salt added (this is only strictly true for small additions of salt); for equal addition to different bloods, dilution of the serum increases with the amount of clot. The salt does not penetrate into the blood-corpuscles, but on the contrary, these probably lose part of their salt.

The action of carbon dioxide on the diffusion which takes place between the serum and the blood-corpuscles in horse's blood increases the specific gravity of the blood, this increase being dependent upon the amount of clot present and the amount of carbon dioxide added. The amount of the solid constituents increases approximately in the same ratio as the change in the specific gravity. The serum loses water and common salt.

Oxygen causes only a slight diminution in the specific gravity of the serum, partly by expelling the carbon dioxide, but most probably, chiefly by causing a diffusion between the blood corpuscles and serum opposed to that caused by carbon dioxide. M. M. P. M.

The Acid of Gastric Juice. By C. RICHET (*Compt. rend.*, lxxxvi, 676—679).—The author has investigated the gastric secretion of certain fish of the genera *Lophia*, *Scyllium*, and *Raja*, the acidity of which (calculated as HCl) was found to be as high as 1 to 1·5 per cent. A comparative estimation of chlorine and of the bases (Na,K and Ca) showed the former to be present in excess of that required by the latter, supposing them to exist as chlorides, in the ratio 3·9 : 1·9.

To ascertain whether this excess of chlorine was present as free hydrochloric acid, an alkaline acetate was added in excess and the whole agitated with ether. By this method, *i.e.*, by a determination of the coefficient of division of the acetic acid liberated, it was found that the amount of the latter corresponded to one-half only of the hydrochloric acid supposed to exist in the free state. Experiments upon solutions of the chlorides of acid amides, such as leucine, alanine, &c., were attended by similar results. From these, and from observations of the rapidity of dialysis, the author concludes that hydrochloric acid exists in the gastric secretion in combination with leucine, tyrosine, and analogous bodies. C. F. C.

Influence of Food on Oxidation. By v. MERING and N. ZUNTZ (*Flüger's Archiv. f. Physiol.*, xv, 634—636).—The process of oxidation in the animal is known to be more active during digestion than during inanition, and is generally supposed to be due to the presence in the blood of the absorbed substances. Might it not, however, be due to the work of digestion and absorption thrown on the alimentary canal and its glands?

Scheremetjewski has introduced a method of distinguishing between these alternatives, by injecting alimentary substances into the blood and examining the exhaled gases both before and after.

The authors' experiments were made on rabbits, the animals throughout the experiments being kept at a normal temperature in a warm bath. The estimation of the gases was made by Röhrig and Zuntz's apparatus. The results were:—

1. Sodium lactate, sodium sebate, glycerin, and sugar, when injected into the blood, were without influence on the absorption of oxygen.
2. Peptone injected into the blood caused an appreciable rise in the absorption of oxygen.
3. Either of the above substances, when brought into the stomach, increased the absorption of oxygen.
4. Substances which pass from the body unchanged, but which excite peristaltic action and secretion (sodium sulphate, mannite), essentially augment the consumption of oxygen.

The peptone, experiments 2, probably acted indirectly by augmenting the activity of the alimentary canal and its glands. The substances in experiments 1 were undoubtedly oxidised, but this action appears to depend entirely on the existing need of the organism.

F. J. L.

Experiments on the Digestive Power of the Horse. By E. Wolff, W. Funke, C. Kreuzhage, and O. Kellner (*Landw. Versuchs-Stat.*, xx, 125—169, and xxi, 19—61).—The experiments described in these papers were undertaken to ascertain, 1st, the digestive power of the horse for fodder of various kinds as compared with that of ruminants; and 2nd, the influence of the work done by the animal on this digestive power. The only observations hitherto published having reference to the horse are those of Haubner and Hofmeister (*Landw. Versuchs-Stat.*, vii, 413, and viii, 99) on the digestibility of meadow-hay and of a mixture of hay, oats, and chopped straw.

The authors have constructed a peculiar kind of stall, which allows of the excrements being collected without loss, as well as an ingenious apparatus, by means of which the animal under experiment may be made to perform an accurately-measured amount of work. Both are fully described.

The first experiments, in which the animal was put through just sufficient daily exercise to keep it in a state of health, were conducted in six consecutive periods, each of fourteen days, during which the daily allowance of fodder was as follows:—

	Meadow-hay. Kilos.	Oats. Kilos.	Wheat-straw. Kilos.	Total dry substances. Grams.
Period I.	10	—	—	8,812
„ II.	8	2	—	8,803
„ III.	12·5	—	—	10,899
„ IV.	8	2	1	9,665
„ V.	6	4	—	8,847
„ VI.	6	4	2	10,571

During the last five days of each period the excrements were collected, weighed, and analysed.

The differences between the amounts of the various food-elements contained in the excrements and those contained in the fodder represented the quantities digested, which were then calculated in percentages. From the formidable array of tabular statements with which the papers are interspersed, the following results may be extracted. The *dried* fodder used in these experiments had the following percentage composition:—

	Protein.	Fat.	Cellulose.	Non-nitrogenous extractive.	Ash.
Hay.......	12·86	3·96	51·56	43·46	8·16
Oats	13·31	6·73	11·05	64·63	4·28
Straw.....	4·57	1·16	46·49	40·27	7·51

Of the constituents of the hay given as food during periods I and III the following mean percentages were digested:—

	Dry matter.	Organic matter.	Protein.	Fat.	Cellulose.	Non-free extractive.
Period I.	55·78	56·84	63·69	42·17	47·21	63·16
„ III.	53·42	53·95	61·75	42·6	44·19	59·77
Mean....	54·6	55·4	62·72	42·39	45·7	61·47

In the successive days of each period, the total weights of the excrements and their composition were remarkably constant. It should be observed that the allowance of hay in period III (12·5 kilos.) was about the maximum that the animal could eat. The weight of the animal was 550 kilos.; calculated for 1,000 kilos. of horse-flesh, the above diets represent—

	Albumin.	Carbohydrates.	Total.
Period I.	1·31	7·45	8·76
„ III.	1·57	8·75	10·32

Assuming that horses performing no work require the same food as oxen of the same weight, the authors calculate that the diet in period I was rather less, and that in period III rather more, than would have sufficed to keep them in a state of health.

In periods II and V the following percentages of food elements were digested:—

	Dry substance.	Organic substance.	Protein.	Fat.	Cellulose.	Non-free extractive.
Period II.	57·37	58·56	69·16	55·24	43·05	64·56
„ V.	63·68	65·57	73·65	60·6	46·33	72·66

Subtracting from the various constituents digested the quantities due to hay alone, calculated on the basis of the results in periods I and III, the authors have determined the digestion-coefficients for oats alone—

	Dry substance.	Organic substance.	Protein.	Fat.	Cellulose.	Non-free extractive.
Period II.	68·45	70·66	94·02	85·47	20·52	72·85
„ V.	77·37	80·29	89·59	76·8	49·04	84·04
Mean....	72·91	75·48	91·81	81·14	34·78	78·45

From these figures it will be observed that the oats were very well digested, as well in fact as by ruminants. Even with the larger allowance in period V scarcely more than 1 per cent. passed unchanged through the alimentary canal.

In periods IV and VI the following percentages of food constituents were digested:—

	Dry substance.	Organic substance.	Protein.	Fat.	Cellulose.	Non-free extractive.
Period IV.	54·87	56·03	69·49	55·67	39·23	62·79
„ VI.	53·53	55·16	68·67	62·73	34·09	62·8

whilst the digestion-coefficients for straw alone are—

	Dry substance.	Organic substance.	Protein.	Fat.	Cellulose.	Non-free extractive.
Period IV.	29·35	30·24	—	—	12·44	44·01
„ VI.	1·54	1·36	—	—	2·48	0

Thus in period IV a considerable quantity of the straw was assimilated, while in period VI, with the larger allowance of the easily digestible oats, nearly the whole of it passed unchanged through the intestines.

During the six periods the variations in the weight of the horse were comparatively slight; at their termination the animal had not lost flesh. The authors therefore collect the results of periods II to VI, and calculate therefrom the absolute weights (in kilos.) of food constituents digested daily per 1,000 kilos. of horse-flesh. Water (including moisture in food) 74, dry matter = 17·63, albumin = 1·506, fat ·431, carbohydrates (including cellulose and non-nitrogenous extractive) = 7·467.

Experiments with sheep were also conducted simultaneously with the foregoing. As a result of these, it was found that the following mean percentage of the proximate constituents of six kinds of meadow-hay, rich in protein and cellulose, were digested, the daily ration being 1,250 grams:—

	Dry matter.	Organic matter.	Protein.	Fat.	Cellulose.	Non-free extractive.
Mean....	63·08	64·65	66·26	63·47	60·51	67·48

Contrasting these coefficients with those determined for the horse (periods I and III, mean), it is clear that, contrary to the generally received opinion, the digestive power of the horse for the protein and non-nitrogenous extractive of the hay here used is not inferior to that of the sheep, whilst considerable differences are observed for fat and cellulose, especially the latter. The ratio of nitrogenous to non-nitrogenous digested matters was, in the experiments with sheep, 1 : 6·4, in those with the horse 1 : 5·63; the lower ratio in the former case being chiefly due to the greater digestive power of the sheep for fat and cellulose.

In other experiments with sheep, the daily food consisted of 1 kilo. meadow-hay and ¼ kilo. oats and of ¾ kilo. hay and ½ kilo. oats, the ratio of oats to hay being the same as in periods II and V of the experiments with the horse. The percentage of each food constituent digested was nearly the same in both series of experiments, the following being the mean coefficients calculated for oats alone:—

Dry substance.	Organic substance.	Protein.	Fat.	Cellulose.	Non-free extractive.
73·03	74·08	86·24	80·72	26·56	78·62

Contrasting these numbers with those determined for the horse (see above), it is evident that a concentrated food, such as well-formed oats, is equally well assimilated by the horse and by ruminants. The same probably holds true for green food (fresh grass), but not for the same fodder in a more advanced stage of growth (straw), which, although apparently not digested by the horse, is largely assimilated by ruminants (oxen and sheep).

In the experiments described in the authors' second paper, the horse was caused to perform a small daily amount of work (= 465,020 kilogrammeters) measured by the dynamometer. The object here was to ascertain whether the digestion coefficients are influenced by the weight of food administered. Lucerne and meadow-hay were accordingly given, separately and in varying quantities, to the horse and to sheep. It was then found that with the horse the digestion coefficients, so far from diminishing, actually increased slightly and regularly with the quantity of fodder taken; with the sheep under the same circumstances they remained nearly constant, the variations not being well marked. Many interesting details are given by the authors, who purpose continuing these experiments. Ch. B.

On the Products of Tissue Metamorphosis contained in the Fæces of Pigs, and their influence on the results of Digestion Experiments. By E. Heiden (*Landw. Versuchs-Stat.*, xx, 180—185).—The ordinary method of determining the digestibility of food does not take account of those constituents of the fæces which are the result of tissue and other changes, for example, epithelium, mucus and bile; and hence a possible source of error. It has already been shown that the error thus introduced may be neglected in the case of the sheep and ox. It is probably of little importance also in that of the pig; as epithelium and mucus are nearly absent from the fæces of that animal, so that it is only necessary to estimate the excreted biliary matters. This the author has attempted to do by making successively ethereal, alcoholic, and aqueous extracts of the fæces. The nitrogen of the ethereal extract is taken as a measure of the contained bile products, the remainder consisting of cholesterin and fat, the latter partly derived directly from the food. In the alcoholic extract, the bile products (cholic and hyoglycocholic acids) are determined by estimating the total nitrogen and sodium of the ash, the latter existing solely in combination with bile acids.

The sulphur of the aqueous extract affords a measure of the taurin, its nitrogen being partly derived from undigested albumin.

The following table gives the digestion-coefficients of the pig for different foods, and also the coefficients as corrected by the author:—

	Milk.		Maize.		Potatoes.		Milk, maize, and potatoes.	
		Cor.		Cor.		Cor.		Cor.
Dry matter	94·59	95·14	90·75	92·47	92·11	94·0	96·96	97·74
Protein	95·72	96·06	88·12	89·82	67·76	72·12	76·49	81·31
Non-nitrogenous matters	98·54	98·9	94·8	95·28	98·34	99·04	96·63	97·18
Cellulose	—	—	42·6	42·6	38·82	38·82	45·56	45·56
Ash	64·54	64·47	32·9	33·54	66·57	67·72	90·64	61·02

Ch. B.

Deportment of the Shells of Hen's Eggs during Incubation. By C. Voit (*Zeits. f. Biologie*, xiii, 518—526).—It is stated on the authority of Prout and others, that the lime necessary for the formation of the skeleton of the young chicken is partly derived from the egg-shell. The author has now ascertained by careful analyses, firstly, that no lime is withdrawn from the shell during incubation, and secondly, that the small quantity of lime (35 milligrams) and other mineral matters contained in the chick is fully accounted for by the mineral constituents of the yolk and albumin of the egg.

It has also been stated that the free phosphoric acid found in the ash of the yolk must be neutralised by the lime of the shell, in order to render possible the formation of alkaline blood. This free acid, however, the author shows to be entirely derived from the lecithin of the yolk. If the yolk be exhausted with ether and alcohol, the remaining white mass gives a perfectly neutral ash. The alkalinity of the blood of the chick is due to the alkalis of the albumin.

Ch. B.

Behaviour of Uric Acid absorbed by the Intestinal Canal of the Dog. By E. Salkowski (*Zeits. f. Biologie*, xiii, 527—529).—A reply to the remarks of Ludwig Feder (same Journal, xiii, 297) on the author's paper on this subject (*Deut. Chem. Ges. Ber.*, ix, 719).

Ch. B.

On the Processes of Decomposition. By M. Nencki (*Deut. Chem. Ges. Ber.*, x, 1032—1034).—The author, alluding to Briegel's work, says that the occurrence of numerous substances (indol, skatol, phenol) in normal urine is now intelligible, as they originate from the albumin in the intestine. Indol is no longer a substance without analogue, for skatol resembles it in all respects in its chemical comportment. Probably, also, skatol as well as indol, is formed by the action of fused potash on albumin.

The author does not believe that injections of indol prepared *exactly* according to his method would have occasioned the excretion of phenol in the urine, and thinks that Salkowski must have used crude indol, as it remains when the ethereal solution is evaporated. He recommends pancreas as the cheapest and most productive source of indol.

E. C. B.

Action of Glycerin on the Animal Organism. By P. Plósz (*Pflüger's Archiv. f. Physiol.*, xvi, 153—156).—The investigations of

Luchsinger having shown that the decomposition of glycerin in the animal organism bears a close relation to the formation of glycogen, additional interest has been given to this subject. It would appear from the author's experiments, that after large doses of glycerin have been administered, a body of energetic reducing power is formed in the urine, which however cannot be isolated.

The urine containing this body reduces alkaline solutions of the oxides of copper, bismuth, and silver, and if the quantity be large, the precipitation of cuprous oxide is immediate; even when it is present in but small quantities, reduction takes place slowly in the cold.

The solution of the new compound becomes brown when heated with soda, resembling grape sugar in this respect. It differs from it however in not undergoing fermentation, and in being optically inactive. It is also apparently more easily split up and more energetic in its reducing power than sugar. It is soluble in alcohol, insoluble in ether.

This substance is probably identical with that obtained by Berthelot from glycerin by fermentation with testicular tissue, and regarded by him as sugar, but shown by others to be optically inactive and unfermentable. Its exact nature is not known, but it is probably an aldehyde of glycerin: this hypothesis would also account for its conversion into glycogen by reduction of the glycerin, $C_3H_8O_3$, into its first aldehyde, $C_3H_6O_3$, and subsequent condensation and separation of the elements of water, whereby the compound $C_6H_{10}O_5$ might be produced.

In large doses glycerin has a deleterious effect on the organism, the results of which have been described by Dujardin-Beaumetz and Audige (*Union Medicale*, 1876). F. J. L.

Physiological Action of Curare-poison. By G. COLASANTI (*Pflüger's Archiv. f. Physiol.*, xvi, 157—172).—The author's experiments tend to show that the power of curare in modifying the processes of oxidation is an indirect action due to its neutralising the influence of the central nervous system on the voluntary muscles.

They also point to the important fact that the central nervous system is a far more powerful exciter of metabolism than is generally supposed. F. J. L.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Glycerin on the Processes of Fermentation. By I. MUNK (*Pol. Notizblatt*, 32, 269, and *Chem. Centr.*, 1877, 678).—The addition of glycerin, the author finds, retards the lactic and alcoholic fermentations. One-fifth of glycerin added to milk at a temperature of 15° to 20° prevents it from turning sour for eight or ten days. One-half or one-third of glycerin at the same temperature postponed the fermentation of milk for six or seven weeks. At higher temperatures larger quantities of glycerin are needed to produce the same results.

The formation of hydrocyanic acid from amygdalin and emulsin is also retarded by glycerin. E. C. B.

Researches on the Intracellular Alcoholic Fermentation of Plants. By A. MUNTZ (*Compt. rend.*, lxxxvi, 49).—Lechartier and Bellamy have shown that certain fruits, leaves and roots, under the influence of oxygen, become the seat of an alcoholic fermentation, characterised by the evolution of carbonic acid, without the appearance in the tissues of alcohol plant-cells. From these and other experiments, Pasteur considered that if plants could continue to live in an atmosphere of carbonic acid, they would become ferments for sugar.

The author has repeated the experiments with some modifications.

The plant, not removed from the soil, was covered with a large bell-glass, and the oxygen removed by means of potassium pyrogallate. Each experiment was performed on three similar plants; the first was left in the open air, the other two were left in the atmosphere of nitrogen for twelve to forty-eight hours. At the end of that time, one of them was examined for alcohol, and the other exposed to the air, to ascertain whether any deleterious effect had been exercised by the nitrogen.

The alcohol in the plants was found by fractional distillation and conversion into iodoform, which was detected by means of the microscope.

It was not thought necessary to search for microscopic organisms which might have produced alcohol; firstly, on account of the short duration of the experiment; and secondly, because the plants which were returned to the air always remained perfectly healthy, which would not have happened if they had contained mycoderms.

The experiments were conducted on vine-branches covered with leaves, on beets in various stages of development (the leaves and roots were examined separately), on maize, cabbage, chicory, purslain, nettles, &c. All the experiments gave the same results.

(1.) The plants preserved in the air gave no trace of alcohol.

(2.) The plants placed in nitrogen gave very appreciable quantities of alcohol, sometimes amounting to $\frac{1}{1,000}$th of the total weight of the plants.

(3.) The plants returned to the air remained perfectly healthy.

These experiments show that the living cell in the higher plants is capable, in the absence of oxygen, of acting like the cells of fungi, in producing a true alcoholic fermentation. C. W. W.

Analytical Chemistry.

A New Substitute for Litmus in Titration. By W. v. MILLER (*Deut. Chem. Ges. Ber.*, xi, 460—461).—Aqueous solutions of William, Thomas and Dower's new colouring matter, tropäoline, exhibit a striking change of colour from yellow to red on the addition of acids.

The author recommends the use of this body as a substitute for litmus in alkalimetry, not only for the delicacy of the above reaction, but also for its being uninfluenced by acid carbonates and free carbonic acid, and also by normal metallic salts, which redden litmus. C. F. C.

Estimation of the Mineral Matter in Paper. By C. WURSTER (*Dingl. polyt. J.*, ccxxvii, 179—184).—A point of great importance in the manufacture of paper is to ascertain the loss of material in its passage from the raw state to that of the manufactured article. The results of a few experiments have been generally adopted in calculating all papers; and although this, in the case of similar kinds of paper, glazed to the same extent, possessing the same colours and same mineral constituents, gives fair results, yet the method is unsatisfactory when the most varied kinds of papers are manufactured from different kinds of materials. For the purpose of cheapening paper, manufacturers have been in the habit of adding large quantities of mineral matter, filling-stuff (Füllstoff) as it is called, to increase the weight, and thereby diminish the price of the paper. A few analyses settled the amount of mineral matter or filling-stuff taken up by papers, and this has been taken in all calculations of price; but, owing to negligence of the workmen, occasionally no filling-stuff is added; moreover varying quantities of it are taken up by paper, dependent on the nature of the pulp, sizing of paper, &c. An analysis of each kind of paper is therefore necessary, not only to fix fairly the price of the paper, but to control the operation of making, so that a negligent workman may be detected if he has forgotten to add the filling material.

The method of determining the ash is to take 1 gram of paper, roll it up, and wind a spiral of platinum wire around it, which spiral is supported by the two ends of the wire in a horizontal position. The paper is then burnt by a spirit lamp over a sheet of paper in the usual way. The water in kaolin and gypsum is not driven out by this method unless the heat be too high, so the ash gives at once the amount of filling matter introduced. The same is the case with tinted papers. The author also proposes analyses of the materials (straw, old paper, &c., and new linen rag) used in making paper, in consequence of the amount of mineral matter, starch, &c., to be found in them. From these analyses a correct view of their value may be obtained. The following are some of the analyses:—

	Dried.	Ash.	
Unglazed paper..................	2·995	0·025	= 0·83 per cent.
Red blotting paper from red rags ..	2·667	0·0215	= 0·83 „
Blue blotting paper from blue rags.	2·579	0·0210	= 0·81 „
Unglazed paper from boiled, but not bleached, coloured rags	2·517	0·027	= 1·07 „
Pine wood	3·175	0·013	= 0·408 „

Woody matter from various factories in form of pulp, dried in air—

1. 2·558	gave	0·0055	ash, or	0·21	per cent.
2. 2·356	„	0·009	„	0·38	„
3. 1·7155	„	0·006	„	0·34	„
4. 1·812	„	0·004	„	0·22	„

Paper with brown glaze, without addition of filling matter—

1. 1·790 gave 0·031 ash, or 1·7 per cent.
2. 2·189 „ 0·038 „ 1·7 „

Paper with white glaze and without filling matter, still dried in air—

1. 2·212 gave 0·03 ash, or 1·3 per cent.
2. 1·549 „ 0·020 „ 1·3 „
3. 0·0505 „ 0·015 „ 1·5 „

S.

Estimation of Copper and Sulphur in Iron Pyrites. By FRESENIUS (*Dingl. polyt. J.*, ccxxvii, 97—98; and *Zeitschr. f. Anal. Chem.*, 1877, 335).—In the analysis of iron pyrites it is advisable to estimate first the moisture in the pyrites and calcined ore, and then to determine the sulphur and copper in specimens dried at 100°.

The determinations of moisture are made at 100°, on 25 grams of pyrites or 10 grams of calcined pyrites, without being pulverised.

Carefully pulverised samples of the pyrites, calcined and uncalcined, are taken and dried at 100°. For the estimation of the copper in the uncalcined ore, 5 grams are warmed in a flask with 6 or 7 c.c. nitric acid of 1·17 sp. gr., and about 20 c.c. of concentrated sulphuric acid are added gradually until the action is over. The ore is digested for some time at a gentle heat, and the contents of the flask poured into an evaporating basin, and evaporated nearly to dryness: 20 c.c. of sulphuric acid (1·12 sp. gr.) are then added. After being warmed it is diluted with water, and filtered into a boiling flask of 500 c.c. capacity. The residue is dried and ignited, and then boiled with *aqua regia*, evaporated to dryness, and treated with 5 c.c. of hydrochloric acid. After dilution, the solution of lead chloride containing copper is filtered off into the 500 c.c. flask, and diluted up to 400 c.c.

Calcined ore is treated thus:—3·5 to 4 grams are heated with 24 c.c. of sulphuric acid and 6 c.c. of nitric, until all the soluble matter is dissolved; the solution is diluted and filtered; the residue washed, dried, and ignited, and boiled with 1 c.c. hydrochloric acid and a few drops of nitric, and evaporated. 2 c.c. of hydrochloric acid are then added, and the solution filtered with the rest. This is diluted to 400 c.c.

The solutions thus obtained are precipitated with sulphuretted hydrogen and filtered. The precipitate is collected, dried, and burnt in the usual way; it is then heated with 5 c.c. of nitric acid of 1·2 sp. gr., diluted, and filtered into an evaporating basin. The residue is washed and again ignited, and heated with 2 c.c. of nitric acid, and filtered into the chief solution. The solution thus obtained is then treated with dilute sulphuric acid (1 : 5), evaporated on the water-bath until all the nitric acid is destroyed; a little water is then added, and the lead sulphate collected on a filter and washed. The copper sulphide is precipitated by sulphuretted hydrogen at 70°, washed, dried, and heated to redness, mixed with sulphur, ignited in hydrogen, and weighed.

In estimating the sulphur in the uncalcined pyrites, 0·5 gram is mixed in a crucible with 10 grams of a mixture of 2 parts of Na_2CO_3 and 1 part KNO_3. A layer of the latter mixture is then spread over the surface, and the whole heated strongly by a flame free from sulphur, such as that of a spirit lamp. When the reaction is complete, the mass is allowed to cool, dissolved in hot water, and carbonic acid passed through to precipitate lead. The solution is filtered, the residue heated with pure soda and filtered. The filtrate is acidified with hydrochloric acid, and evaporated several times with the same acid to get rid of the nitric acid. The residue is then moistened with hydrochloric acid dissolved in boiling water and filtered, and the sulphuric acid precipitated by barium chloride in the usual way.

When calcined pyrites is taken, 1 gram is fused with 5 grams of a mixture of 4 parts Na_2CO_3 and 1 of KNO_3. S.

Estimation of Silver and Gold in Cupelled Silver. By O. LINDEMANN (*Dingl. polyt. J.*, ccxxvi, 66—70).—The author employs the thiocyanate method of determining the silver, and the the entire process may be described thus:—About 10 grams of granulated silver are weighed out and placed in an assay flask of 250 c.c. capacity. 50 c.c. of nitric acid free from chlorine are added, and the whole heated until red fumes cease to come off. When the gold has settled to the bottom the silver solution is poured into a litre flask. More nitric acid is added to the gold, and heat applied. This is also decanted into the litre flask. The gold is then carefully washed with distilled water until the decanted fluid gives no trace of silver. The assay flask is then filled with water, a porcelain crucible placed over it, and the whole inverted.

The gold settles into the crucible, and with practice, by carefully removing the flask, the gold can be left in the crucible. It is then dried and weighed. The litre flask containing the silver solution is filled up to one litre exactly, 50 c.c. are taken, and the silver is estimated with a normal solution of potassium thiocyanate.

To ensure accuracy, the same pipette and burette and the same litre flask are always employed, both with the test solution of silver for titration of the sulphocyanide, as well as for the analyses. The author gives examples of analyses. Nos. 3 and 5 contained some lead, and this interfered with the estimation of the silver.

Silver used dissolved to 1000 c.c.	Yield of gold.		Amount of sulphocyanide used to 50 c.c. of sol. 100 c.c. KCSy = 0·99356 of silver.	Silver in the 50 c.c. employed = $\frac{1}{20}$ of that contained in the quantity dissolved.	
Grams.	Mgm.	Per cent.	c.c.	Mgm.	Per cent.
9·9804	28·9	0·289	47·2	468·96	93·976
10·0060	30·3	0·302	47·2	468·96	93·735
10·0414	73·6	0·732	43·5	432·20	86·083
10·0046	32·1	0·320	47·85	475·42	95·039
10·9544	23·4	0·232	46·35	460·52	91·604

The Value of Cupric Acetate (and Formate) as a Delicate Test for Grape-sugar. By W. Müller (*Pfluger's Archiv. f. Physiol.*, xvi, 551—561).—Barfoed has shown (this *Journal* [2], xi, 1163) that a solution of cupric acetate is reduced by grape-sugar at the ordinary temperature, and that in the presence of free acetic acid it can be used at a boiling temperature to detect grape-sugar when occurring with dextrin, milk-sugar, and cane-sugar.

The author has examined the delicacy of this test, with the primary object of applying it to the detection of grape-sugar in urine. With pure grape-sugar and an aqueous solution of cupric acetate, the reaction is not sensitive at the ordinary temperature. It is very delicate at 45°, when a 4 per cent. solution of cupric acetate will detect ·000234 gram of grape-sugar in 3 c.c. of liquid, or $\frac{1}{128}$ per cent. The reduction, however, is slow, about 20 hours being required to show this quantity of sugar.

The results obtained by Barfoed are confirmed as to the delicacy of the reaction which occurs between grape-sugar and an acetic acid solution of cupric acetate. The action of dextrin, &c., on this solution was not examined.

The original test is thus modified. The grape sugar solution is boiled for $\frac{3}{4}$—2 minutes with $\frac{1}{2}$—1 c.c. of a solution containing 4 per cent. of cupric acetate and 1 per cent. of free acetic acid. Prolonged boiling must be avoided. Thus followed, the test will readily detect $\frac{1}{16}$ per cent. and even $\frac{1}{32}$ per cent. of grape-sugar. Cupric formate is of no value as a delicate test for grape-sugar. A. J. C.

Behaviour of Normal Urine to Cupric Acetate and Sulphate, and to a Solution of Cupric Acetate Containing free Acetic Acid. By W. Müller (*Pfluger's Archiv. f. Physiol.*, xvi, 562—566).—Normal urine contains substances other than uric acid and the alleged trace of sugar, which are capable of reducing cupric acetate and sulphate at the ordinary temperature, and an acetic acid solution of cupric acetate at a higher temperature, thus rendering these reagents of no value as a means of detecting grape-sugar in urine.

A. J. C.

Volumetric Estimation of Sugar in Human Urine and in Animal Liquids. By W. Müller and J. Hagen (*Pflüger's Archiv. f. Physiol.*, xvi, 567—603).—Knapp's method for determining sugar is preferred by the authors to all others. The standard liquid is prepared by dissolving 10 grams of pure, dry, mercuric cyanide in water, adding 100 c.c. of sodium hydrate solution, sp. gr. = 1·145, and diluting to 1000 c.c.: 10 c.c. = 25 mgm. grape-sugar.

10 c.c. of the liquid, diluted with 20—30 c.c. water, are heated to incipient boiling; the urine (diluted generally five or ten times) is run in from a burette, until the whole of the mercury is precipitated. When the precipitate has settled, a drop of the supernatant liquid, which has a more or less yellow tint, is transferred by means of a capillary tube to a piece of *thin*, *pure-white* filter paper (fine Swedish is to be preferred). The paper is held, first, over a bottle containing strong hydrochloric acid, and then over concentrated sulphuretted hydrogen solution. The slightest trace of mercury is shown

by the production of a light-brown or yellow stain. It is well to place a drop of the original liquid beside that which has been subjected to the action of hydrochloric acid and sulphuretted hydrogen, for comparison. In this way it is easy to detect the very slightest trace of mercury in solution in the liquid. By comparing Knapp's process with Fehling's in the case of urines containing so much sugar that no cuprous oxide remained in solution after filtration, it was found that both were equally applicable and equally exact; but when the amount of sugar fell below 0·5—0·7 per cent., Fehling's process ceased to give trustworthy results: on addition of the urine, the test-liquid became turbid, then greenish, then of a sherry-brown colour, and finally exhibited a faint yellowish opalescence by reflected light. The sherry-brown colour was due to dissolved cuprous hydrate, the opalescence, to finely-divided particles of the same substance, which remained suspended in the liquid, and could not be removed by filtration, even after the liquid had remained at rest for hours. There is a certain limit in the amount of sugar, above which a clear, and under which a turbid filtrate is invariably obtained in the use of Fehling's method. This limit is about 0·5 per cent. Knapp's method, on the other hand, is available for exact determination when the amount of sugar falls to 0·1 per cent., or even less. Attempts were made to render Fehling's method applicable for urine containing less than 0·5 per cent. of sugar by diluting the urine considerably, and thus decreasing the relative amount of those substances which prevent precipitation of the cuprous hydrate, but the results were unsatisfactory. It is, however, true that cuprous hydrate settles more readily in a dilute, than in a concentrated liquid, other things being equal.

Claude Bernard has supposed that by varying the amount of alkali in Fehling's liquid, good results might be obtained with urines containing varying amounts of sugar. The authors find that by decreasing the amount of alkali, the amount of suspended cuprous hydrate, relatively to that held in solution, increases; but that by varying the alkali, the limit of sugar below which the method of Fehling ceases to give satisfactory results is not materially altered.

The addition of lead acetate, to carry down the suspended cuprous hydrate, was tried, but without satisfactory results. If too much acetate is added, portions of the sugar are liable to undergo precipitation; if too little, the cuprous hydrate remains in suspension.

The reason why a clear filtrate, free from cuprous hydrate, is obtained in Fehling's process, only when the amount of sugar passes a certain limit, is to be found in the *relation* between the amounts of sugar and of those substances which dissolve, or prevent precipitation of cuprous hydrate. The exact nature of these substances has not yet been determined.

Generally speaking, diabetic and non-diabetic urines, containing sugar, show no marked difference in their behaviour towards Fehling's liquid. As a general rule, diabetic urine can be titrated by Fehling's method when containing less sugar than could be exactly determined by the same process in a non-diabetic urine. This reason of this, according to the authors, is the presence of "polyurie," which may be present in urine containing very little sugar. The presence of "polyurie" is proved by the authors' experiments to render titration easy. The authors differ on this point from many eminent physiological chemists, who held that those substances which prevent the precipitation of cuprous hydrate are present in very small quantity in diabetic urines. This explanation is in accordance with the fact, that those urines which readily reduce Fehling's liquid are light-coloured, whilst other urines have a dark colour. But this difference in colour is due—say the authors—merely to a difference in concentration. If the amount of sugar fall below a certain limit, and if "polyurie" be absent, an exact determination of the sugar by Fehling's process is not possible, no matter what the colour of the urine may be.

In diabetic urine, the limit of sugar is lower because the urine is abnormally diluted, and hence all substances other than sugar are present in relatively smaller quantity than in normal urine. If normal urine be diluted, the *proportion* of sugar to other substances remains unaltered.

Knapp's method is to be preferred to that of Fehling for the following reasons; the test-liquid is very easily prepared; it does not alter on keeping; the method is applicable in all cases; the mercury settles quickly, and does not again redissolve (cuprous hydrate frequently passes into solution after precipitation), and no filtration is required. (Direct experiments of the authors show that many filtering papers, on treatment with warm water, yield a liquid which reduces Fehling's solution.) Knapp's process renders it possible to determine the total amount of reducing substances in urine. It does *not* determine the *sugar only;* for the purpose for which it is designed, the process is as good as can be desired. Bodies other than sugar, possessing the power of reducing both Fehling's and Knapp's liquids, are generally present in animal liquids; but the exact amount of these bodies in urines and in other liquids is not known: exact information on this point is a desideratum. The authors' experiments on alcoholic solutions of the muscles of a diabetic subject showed the presence of about 0·3 per cent. of a substance or substances, capable of exerting reducing action on the test-liquid: sugar was absent from the muscular extracts examined.

Both Fehling's and Knapp's methods are applicable to the determination of sugar in urine containing not more than 0·2 per cent. of albumin. If very exact results be required, it is, however, better to remove the albumin before titration; Knapp's method gives better results than Fehling's. If the amount of albumin exceed 0·2 per cent., titration by Fehling's process becomes impossible, because cuprous hydrate remains suspended in the filtrate and cannot be removed. Knapp's process is still applicable under these conditions, but the mercury settles very slowly. It is, therefore, always advisable to remove albumin when present in quantity exceeding 0·2 per cent., before determining sugar by either process.

M. M. P. M.

Estimation of Nitrogen in Plant Albuminoïds. By H. Ritthausen (*Pflüger's Archiv. f. Physiol.*, xvi, 293—301). — The author has carefully tested the methods of Dumas and of Will and Varrentrapp. The former alone gives satisfactory results. The analyses were carried out in a stream of carbon dioxide, produced by heating acid sodium carbonate, and purifying the gas.

M. M. P. M.

Estimation of Acids in Oil. By E. GEISSLER (*Dingl. polyt. J.*, ccxxvii, 92—93).—The oil to be tested is diluted with twice its volume of ether, a drop or two of *rosolic acid* added, and the amount of acidity determined by titration with a standard solution of potassium hydrate.

S.

Analyses of French Wines. By E. HOUDART (*Bull. Soc. Chim.* [2], xxvii, 551—553).—The paper is accompanied by a table giving the analyses of a number of French wines. The author remarks that the weight of extract obtained is affected by the mode of drying, the time, and even the nature of the vessels. Thus, the same quantity of the same wine dried during the same length of time and in vessels of the same capacity, yielded the following weights of extract in the different vessels:—In thick porcelain dish, 19·60; in platinum dish, 18·08; in platinum dish with calcined flint, 16·74.

R. R.

Technical Chemistry.

Soda Manufacture. By W. WELDON (*Chem. Centr.*, 1878, 109—110).—Sodium sulphate is melted in a Siemens' regeneration furnace, and poured on to the requisite amount of red-hot coal contained in a revolving furnace, the inside of which is protected from the action of the molten sodium sulphide by a thick layer of compressed magnesia, coke, or graphite. The carbon dioxide set free during the process is collected in gasometers, and used in the manufacture of sodium bicarbonate. The sodium sulphide is converted into caustic soda by the action of superheated steam. The silicate and phosphate of soda are made by heating a mixture of the sulphide with silica, or with aluminium phosphate, in a current of superheated steam.

Sodium bicarbonate separates out, when carbonic acid is passed into a cold solution containing 12·20 per cent. of sodium sulphide. The carbonate is obtained by calcining the bicarbonate.

W. C. W.

Soluble Glass. By R. MEYER (*Dingl. polyt. J.*, ccxxvii, 280—289).—The author proposes the application of soluble glass for scouring of cotton goods, in order to remove fatty and other matters before dyeing. A very dilute solution acts much more energetically than a relatively concentrated soda solution. The application of clay is rendered unnecessary, and the time occupied by the process is much shortened.

The author has examined Liebig's process for the preparation of soluble glass by treating infusorial earth with potash or soda-lye. Three samples of infusorial earth from (A) Lüneburg, (B) Unterlüss, and (C) unknown locality, respectively were examined by heating with soda lye and the dissolved silica determined.

A. Washed, white, 71·4 per cent.; unwashed, 62·3 per cent; "green infusorial earth," 44·4 per cent.
B. Washed, white, 76·7 per cent.; unwashed, white, 58·0 per cent.; unwashed, grey, 44·2 per cent.
C. Washed, white, 76·4 per cent.; unwashed, white, 59·8 per cent.; unwashed, grey, 48·7 per cent.

Two samples of soluble glass were analysed, with the following result:—

	I.		II.
Na_2O ……..	6·68		9·8
SiO_2 ………	23·29		26·1
H_2O ………	67·54		62·4
NaCl ……..	0·54	by diff.	1·7
Na_2SO_4 ……	0·60		
$Al_2O_3 + Fe_2O_3$	0·60		
	99·25		100·00
Sodium silicate	29·97		35·9 corresponding to
SiO_2…… ..	77·7		72·7
Na_2 O…….	22·3		27·3
	100·0		100·0

Attempts were made to form a silicate as rich in silica as I by heating an excess of infusorial earth with soda-lye; the highest silicate obtained contained SiO_2 73·86, Na_2O 26·14. When amorphous silica in excess was used, very acid silicates containing 79·79 and 80·90 per cent. of silica respectively were produced. This shows that the insoluble constituents of infusorial earth act prejudicially in preventing the solution of the silica. J. T.

Notes from the Laboratory of the Riga Polytechnic. By M. Glasenapp (*Dingl. polyt. J.*, ccxxvii, 192—196).—1. *Employment of Calcined Dolomite for taking Casts.*—The dolomite experimented on was taken from the Middle Devonian, which is well developed in South Livland and Kurland. When dolomite is burnt to such an extent that the magnesium carbonate only is decomposed, a fair mortar is the result. Experiments with the East Baltic (Livland, &c.) dolomite gave an unsatisfactory result, as the mortar did not set well. The composition of the dolomite was as follows:—

$CaCO_3$.	$MgCO_3$.	$FeCO_3$.	Al_2O_3.	Silicate and sand.	
55·23	41·64	0·58	0·12	2·63	= 100·20.

In further experiments the dolomite was calcined until all the carbonic acid was expelled. When the product was pulverised and mixed with water, it united readily with it after the lapse of five or ten minutes, with development of much heat, and set so firmly that it could not be scratched by the finger-nail. When proportions of 100 of calcined dolomite to 70 of water were mixed, the temperature rose from 15° to 75°. The water and dolomite can be mixed to such a consistency that it may easily take the place of gypsum for taking casts. The cast cannot be removed for some days, as the setting occupies some time.

2. *Production of a Black Oil Paint for Wood and Iron.*—100 parts by weight of linseed oil varnish, made from lead preparation, are heated, and then 15 parts of litharge or red lead slowly added. When this is dissolved by aid of stirring, 1·5 parts of flowers of sulphur are thrown in, and the whole constantly stirred to cause the union of the lead and sulphur; then 2 parts of litharge are again added. After cooling, the paint is diluted by admixture of turpentine to the proper consistency. The paint has a good covering power or body, and the colour is somewhat grayish in appearance. It is necessary to have excess of lead, and the above proportions ensure this.

3. *Formation of Ammonium-magnesium Sulphate in Gas Purifying.*—The author's attention was directed to stalactites in a cellar at the gas works of Riga, and he found these stalactites, which were yellowish-white and transparent, to have the following composition:—

MgO.	$(NH_4)_2O$.	SO_3.	H_2O (difference).	
10·96	14·28	44·53	30·23	= 100·00

This corresponds to the salt $(NH_4)_2SO_4.MgSO_4 + 6H_2O$. The lime used in purifying contained large quantities of magnesia, and from this source the magnesium in the salts was derived. S.

Cohesive Power of Clays. By C. Bischoff (*Dingl. polyt. J.*, ccxxvi, 195—205).—The cohesive power (Bindevermögen) of clays rests on their power of taking up pulverised or large-grained portions of foreign matter after it has been moistened with water, and forming a substance of certain strength and structure on drying. This power can be estimated only by experimental methods. One method is to mix the dry clay with 1, 2, 3, &c., times its volume of fine quartz powder, which must be of an equal degree of fineness. After thorough mixing, the results are formed into small cylinders, which are then dried and numbered 1, 2, 3, &c., according to the amount of sand added. The cylinders when cold are then rubbed gently with the index finger, and at last one cylinder is obtained which allows of small portions or grams to be rubbed off. This number expresses the agglutinative power of the clay. This method is open to the objection that it is the pressure of the finger which operates, and not the resistance of the clay, so that an incorrect result is obtained. Beurath (*Glasfabrikation*, p. 78) proposes a horsehair pencil as a substitute. The author has improved on this by suggesting a brush of pig's bristles. This receives a quick backward and forward motion by being placed on an axle worked by a wheel and the foot. The axle instead of receiving a rotatory motion moves alternately in one direction and then in the other. The cylinders are presented to the brush in such a way that each receives the same pressure of the brush and an equal number of touches.

0·16 grams of clay are weighed out, and 1, 2, 3, &c., times its weight of pulverised sand, &c., added. The best Belgian clay was taken, and mixed with 10, 20, and 30 per cent. of poorer clay, viz., Saarau clay, sifted through a mesh of 1,296 per square centim. After drying at 100° and thoroughly mixing, 0·16 g. of each was taken and mixed with 10, 11, 12, 13, and 14 times its weight of sifted sand. The cylinders were then formed and dried at 100° to 120°. The amount of water to be added must be carefully regulated, but this comes by practice. The clay must mould easily, but must not be too soft. The cylinders were rubbed with a pencil of pig's bristles, which was 2 cm. long and 1 cm. broad at the widest end. Each article received 50 strokes of the brush. The results were:—Clay without addition of Saarau clay: Nos. 10, 11, and 12 showed no signs of attack, or at least signs of but very faint action. Nos. 14 and 15 showed a slight concave surface when the brush had passed, and this surface being accepted as the criterion, the agglutinative power of the clay was set at 14 to 15. This new method gives a higher figure than the older methods, and so enlarges the scale for testing clays.

Clay with 10 per cent. admixture gave No. 13 as a result. So 10 per cent. admixture of a less good clay is perceptible by a decrease of 2 in the scale.

The sample with 20 per cent. of Saarau clay gave 11 to 12 as the number. The sample with 30 per cent. gave 10.

By this method the decrease in the quality of clay by 10 per cent. is easily perceptible.

The agglutinative power of other clays was determined by this method, and gave—

For Saarau clay, 3.	Zettlitz kaolin.
Class II gave 6—7.	Mühlheim clay.
„ IV „ 14.	Grünstadt clay.
„ V „ 12.	Clay from Oberkaufung.
„ VI „ 13.	Niederpleiss clay.
„ VII „ 11.	

Another method is to estimate the quantity of water taken up by the clay. Clay is placed on a filter and water poured over it; the excess of water can flow off. The result is then dried for an hour over sulphuric acid. Experiments by the author seem to show, however, that the quantity of water taken up by the clay bears no direct relation to its agglutinative power, as some clays with less agglutinative power absorb more water than those with more.

The author then mentions some methods carried out in practice. A bullet is made of clay, and this has to be pressed to half its diameter before cracking at the circumference. Threads or strings are forced through holes, and the length of the string before it breaks is the test of its cohesive power; or a long cylinder is formed into a ring, which must not crack in the process. S.

Electrolytic Deposition of Nickel. By R. KAYSER (*Chem. Centr.*, 1878, 127).—The objects on which the nickel is to be deposited must be carefully cleaned, and placed in a bath containing 1 part of the double sulphate of nickel and ammonium to 20 parts of water. The nickel salt must be pure, and also the nickel anode, which should not be smaller than the article to be plated, and a strong current should be used. If the bath gets acid it must be neutralised by the addition of dilute ammonia. In plating copper articles, the bath should contain 1 part of ammonium chloride to 100 of the nickel salt.

W. C. W.

Silver Plating. By ROSELEUR (*Chem. Centr.*, 1878, 143).—Precipitated silver chloride mixed with eighty times its weight of cream of tartar is added from time to time to boiling water contained in a copper vessel, in which the articles to be plated are immersed. If the bath does not work well, the articles are immersed for some seconds in a boiling solution of 100 grams silver nitrate, and 600 grams potassium cyanide, in 10 litres of water. This both increases the lustre and whiteness of the articles.

Paste-plating.—The paste is prepared by grinding with a muller the following substances in the dark:—

Silver nitrate	100 grams.
Acid potassium oxalate	300
Cream of tartar	300
Sodium chloride	420
Ammonium chloride	80
Water	100—150

or thus—

Silver chloride	60
Cream of tartar	200
Sodium chloride	300

To apply this, a portion of the paste is mixed with a little water and painted on the object to be plated, which must have been previously covered with a layer of gold so thin that the copper beneath can decompose the paste applied. After drying, the rose or green coloured paste is washed off in cold water. The whiteness and lustre are increased by immersion for a few seconds in a potassium cyanide solution. This plating will bear the scratch-brush and polishing, and also oxidising; in these respects the method is superior to that first described.

J. T.

Phosphorus in Copper. By A. LISMANN (*Dingl. polyt. J.*, ccxxvii, 278—280).—The author, in order to guard against the bad effects of overpoling, wraps amorphous phosphorus in thin sheet copper, and stirs it into the bath of molten copper before toughening. Experiments were made on a charge of 5,000 kilos. of Chili copper, with the following results:—

	Tenacity, kilos. per square c.m.	Elongation, per cent.
I.	1920	14·5
II.	1870	14·5
III.	2180	21·8

I is the copper without admixture of phosphorus.

II was prepared by strewing 200 grams of amorphous phosphorus upon 285 kilos. of the copper as it was being cast. This shows that the test piece did not differ from I.

III was prepared as described above, by adding 1·5 kilos. of phosphorus in ten portions, each wrapped in sheet copper, to about 1,400 kilos. of copper, and incorporating by stirring. The tenacity was thus increased by one-eighth, and the product was quite free from honeycombing. J. T.

Russian and American Kerosin and the Employment of Heavy Mineral Oils in Lamps. By K. LINENKO (*Dingl. polyt. J.*, ccxxvii, 78—82 and 161—166).—The district surrounding Baku, a city on the borders of the Caspian Sea, is the seat of the petroleum industry of the Caucasus. The regular extraction of this oil commenced in 1872, and 65,000 tons of kerosin from 200,000 tons of raw petroleum is the annual production of this district at the present time; but it could be greatly increased if there were more facilities for land transport, and if the oil compared more favourably with the American than it does. The crude oil of this district comes from springs not more than from 90 to 120 meters deep, and has a sp. gr. of 0·860 to 0·875; it yields only 33 to 35 per cent. of oil for lighting purposes; the remaining naphtha-residue has lately come into request for raising steam in the steam-ships of the Lower Volga and the Caspian Sea.

The refined oil of Baku is distinguished from the American by its higher sp. gr. at 14°, the former being 0·820, the latter 0·800. This would not of itself be prejudicial, but it gives a smoky flame in the lamps.

The author has made researches on the American and Russian oils, and gives the results. Three kinds were experimented on. The 3rd kind is the heavy kerosin, manufactured for Persian consumption; the 2nd is an ordinary commercial variety; while No. 1 is prepared in small quantities only. No. 2 is a clear and slightly fluorescent liquid with a not disagreeable odour. The American varieties tested were of two kinds—1st, the ordinary variety, of a yellow colour; and 2nd, the high test. It also goes by the name of Australöl and Oleophin. These were fractionally distilled under the same conditions with the following results (p. 540):—

From the table it can be seen that the hydrocarbons in the Russian oil are more volatile than those in the American. None of them have been obtained in a pure state.

The author notes that the tar from the gas works at Kasan contains large quantities of benzene, anthracene, &c., and suggests that it could be worked up for colours. From his experiments he thinks that it will be impossible to get an oil from Russian petroleum equal to the American, and suggests that the lamps in which Russian oil is burnt should be made to suit the oil, as the oil cannot be made to suit the lamps. The author instituted many experiments with this view, and found that the bad qualities of heavy kerosin burn with a red and smoky flame in ordinary lamps, and as it does not pass easily up the wick, the flame grows gradually smaller and the wick requires frequent snuffing. Lengthening the glass cylinder caused the flame to become of a brilliant white, but it was not otherwise improved. By diminish-

	Baku No. 3.	No. 2.	No. 1.	Ordinary Kerosin Baku.	Australöl.	Ordinary American Oil.
Specific gravity	At 16·5°. 0·842 At 2·5°. 0·854	At 14°. 0·822 At 2·5°. 0·831	At 19°. 0·801 At 2·5°. 0·815	At 14°. 0·822 At 2·5°. 0·832	At 14°. 0·788 At 2·5°. 0·794	At 16°. 0·795 At 2·5°. 0·804
Percentage distillate at 200°	—	33·4	65·6	31·2	37·8	25·0
" " 280°	76·4	80·4	92·6	80·4	85·0	52·8
Specific gravity of distillate at 200°	—	At 20°. 0·787	At 20°. 0·790	At 18°. 0·789	At 20°. 0·766	At 19°. 0·753
" " 280°	At 19°. 0·835	At 20°. 0·831	At 19°. 0·822	At 18°. 0·832	At 20°. 0·785	At 19°. 0·786
Percentage of distillate at 100°	—	—	—	—	—	—
From 100° to 120°	—	(Boiling-point)	0·1 (Boiling-point)	(Boiling-point)	—	(Boiling-point)
" 120° to 140°	—	0·8	0·6	0·8	—	0·8
" 140° to 160°	—	7·8	24·9	8·8	0·2 (Boiling-point)	6·6
" 160° to 180°	—	21·2	48·0	20·8	3·0	16·0
" 180° to 200°	Boiling-point	33·4	65·6	31·2	27·8	25·0
" 200° to 220°	13·6	45·0	76·6	44·0	48·0	30·2
" 220° to 240°	38·8 (Yellow)	57·8	84·2	56·2	63·8	34·8
" 240° to 260°	62·0 (Yellow)	70·0 (Colourless)	88·8 (Colourless)	69·6 (Colourless)	75·2	44·2 (Yellowish)
" 260° to 280°	76·4 (Yellow)	80·4 (Yellowish)	92·6 (Colourless)	80·4 (Yellowish)	85·0	52·8 (Yellow)
Residue	20·8 (Brown)	15·6 (Golden-yellow)	2·6 (Golden-yellow)	14·8 (Golden-yellow)	11·8	41·8 (Brown)
Loss	3·3	3·0	4·8	4·8	3·2	5·4
Evaporating point	Not determined	28°	25·5°	Not determined	52·2°	28·5°

ing the distance between the edge of the burner and the constriction from 18 mm. to 14 or 16 mm., oil of even 0·887 sp. gr. could be burnt with good results. Wagner and Goldschmidt of Berlin, and also Tänzler of the same city, have constructed lamps which allow of the depression of the cylinder by a screw; but even with these improvements the heavier kerosins do not burn well, probably on account of the wick. This difficulty may perhaps be overcome by altering the construction of the oil holder.

The Möhring lamp, in which an ordinary cylindrical or conical glass without a constriction is used, will burn the heavier kerosins if a cap be placed at a short distance above the edge of the burner. The opening in the cap must be situated at a less distance above the burner than the constriction would have been, as otherwise the flame will smoke. In flat-wick lamps no special results were obtained. S.

Acidity of Beer. By GRIESSMAYER (*Dingl. polyt. J.*, ccxxvii, 93—96).—This is the result of an examination into the qualities of different varieties of beer, to determine what degree of acidity should be allowed to pass by the Government.

The annexed table gives mean results of many analyses, and in the last column the acidity-quotient or the percentage relation of the acid to the extract or solid matter is given:—

Kinds of Beer.	Extract.	Lactic Acid.	Normal Alkali used.	Acidity quotient.
	Per cent.	Per cent.	c.c.	
Pschorr lager-beer	6·4	0·23	2·55	3·593
Spaten „	6·16	0·20	2·22	3·246
Pilsner Bürgerlich. Bränhaur.	4·55	0·13	1·44	2·857
Weihenstephan export	5·75	0·15	1·66	2·608
L. Ahren's Berlin	4·67	0·169	1·18	3·618
.. pastenrisirt.	4·59	0·170	1·90	3·7
Hofbräuhaus (10th July, 1877)	5·43	0·16	1·77	2·946
Bass's pale ale	5·99	0·13	1·44	2·17
Barclay and Perkins's stout	7·41	0·32	3·55	4·318
Salvator, 1875	9·078	0·27	3·00	2·274
Lambic, 1869	2·95	1·116	12·40	37·83
Schwechat lager, 1875	6·01	0·134	1·50	2·229
Pilsner „ „	4·82	0·178	1·97	3·697
Liesing „ „	6·04	0·15	1·66	2·483
St. Max, Märzen „	6·42	0·11	1·22	1·71
St. Max, Abzug „	4·87	0·10	1·11	2·053
Münchener Bock	7·1	0·18	2·00	2·535
Kulmbacher export	7·38	0·16	1.77	2·535
Nürnberger	7·05	0·17	1·90	2·411
Ale	4·81	0·31	3·44	6·444
Porter	7·43	0·34	3·77	4·576
Stout (Guinness)	6·626	0·63	7·00	9·50
Stout (Salt)		0·378	4·20	

The acid was determined by a tenth-normal solution of alkali, and all the acids are assumed to be lactic acid, so that 1 c.c. of normal-alkali solution = 0·09 of lactic acid, 100 c.c. of beer being taken for the experiment.

From the table it will be seen that the mean acidity-quotient for German beer is 2·869, whilst for English beer and stout it varies from 2·17 to 9·5. The Belgian beer is uncommonly sour, and can only be drunk by natives. As the result of these analyses, the author, after excluding foreign beers, divides the German beer into two classes, lager or keeping-beer, and schenk- or draught-beer. The former should have a quotient 3·8, the latter 1·9. All beer overstepping these limits should, he thinks, be condemned and the sellers be liable to a penalty. S.

Preparation of Artificial Champagne. By R. HENNIG (*Chem. Centr.*, 1878, 110—112).—Genuine French champagne contains—

Free acids.	Alcohol.	Sugar.	Glycerin.	Extractive matter.
0·6	8·5	8·5	0·8—1·0	12·5 per cent.

For the manufacture of artificial champagne a wine of the Rheinpfalz Rheingau or Neckar is carefully freed from albuminoïds by the addition of tannic acid. Sufficient gelatin is then added to precipitate nine-tenths of the tannic acid. The wine is left at rest for eight days, then filtered through kaolin and charcoal, and flavoured by the addition of sugar, tartaric acid, glycerin, and cognac or spirits of wine. To impart an agreeable aroma to the wine, extracts of violet, celery, heliotrope, jasmine, and jonquilles; vanillin, cumarin, oil of bitter almonds, and orange-blossom water may also be employed. The flavoured wine is filtered and saturated with carbonic acid under a pressure of five atmospheres. If a red wine is desired an alcoholic extract of bilberries is added. Sometimes the wine is not sufficiently "crêmant;" this can be remedied by the addition of gum arabic and more glycerin. W. C. W.

Nitrobenzene in Spirituous Liquors. By H. G. DEBRUNNER (*Chem. Centr.*, 1878, 157).—The author examined several samples of so-called genuine brandy which smelled strongly of bitter almonds. On distilling 250 c.c. on a water-bath, the residue was turbid and had a very strong odour of bitter almonds. Agitation with ether gave a liquid which yielded a yellow oil on evaporation, consisting of a mixture of nitrobenzene and amylalcohol. The presence of nitrobenzene was confirmed in various ways, as by converting it into azoxybenzene, aniline, &c. J. T.

Coloured Sago. By G. C. WITTSTEIN (*Dingl. polyt. J.*, ccxxvii, 93).—The author finds that the pearl sago manufactured in Europe from potato-starch is coloured with iron oxide. The sago contained 0·7 per cent. of ash, of which 0·4 was iron peroxide. S.

Testing Orange-flower Water. By E. HOFFMANN (*Arch. Pharm.* [3], ii, 229—232).—The red colour which is often produced in orange-flower water during dispensing is found to be due to minute suspended particles of some conifer. Spectroscopically the colouring matter resembles that of *Phytolacca decandra* and *Beta vulgaris*; moreover, the colouring matter of these is changed to light yellow by alkalis, which would be invisible when largely diluted, and to red by dilute acids, which also happens when orange-flower water is added to certain acid medicines. By filtration the water loses the property of becoming red. E. W. P.

Iron Salts as a Substitute for Tan in Dressing Hides. (*Dingl. polyt. J.*, ccxxvii, 86—92, and 185—190.)—This memoir is the result of three years' investigation into the possibility of replacing the ordinary substances used in tanning by salts of iron. It commences with a short account of the nature and object of tanning. It is stated that tanning is a species of dyeing, but with a different object in view—a result of surface attraction for different bodies, as tannin, &c., rather than any result of chemical affinity. The moist tissue of hides left without any preparation becomes rapidly decomposed; and if dried they become stiff and inelastic, in consequence of the filaments cohering strongly together. The object of tanning is to enclose each filament in a coating of matter which will prevent this cohesion. The coating of tanning also protects the filament or cell from decay. Many substances which must be colloidal or amorphous, possess this property, but few of them are capable of producing a useful leather.

Recent studies and investigations have proved that certain salts of iron are capable, both on account of their physical and chemical properties, as well as on economic grounds, of being used for tanning. The preparation which gives the most satisfactory result is, according to the description in the patent, produced in the following manner:—As much nitric acid is added to iron sulphate as is necessary for its complete oxidation. When the evolution of gas ceases, more iron sulphate is added until the evolution of gas, which again takes place, ceases. The solution is now of a yellow-red colour, and more or less syrupy. On slow evaporation, a clear, transparent, deep reddish-yellow varnish, with a shade of orange, is left. The salt in this state has different qualities to that which comes into commerce. This latter salt is decomposed by boiling with water, whereas the one described above can be boiled even in solutions of 30° to 40° B. Moreover it possesses the great advantage of being taken up to a greater degree by hides. The thickest hide can be completely tanned within 72 hours by this preparation. The cost of material was 15*s.* 3½*d.* per cwt., and the whole of the salt is useful for tanning. Vegetable tanning matters, which contain about 15 per cent. of active ingredient, costs £2 0*s.* 9*d.* per cwt., or about 2½ times as much. The most difficult hide can be tanned within a week by the iron method, whilst the ordinary methods take by the American system eight months, by the German, eighteen months.

The only difficulty at first was the production of an article with a good colour. The first experiments gave a leather with a red colour, but a solution of sufficient strength was made, which gave the proper fawn-yellow colour to the leather.

The influence of this material on the weight of the leather was the next question; and in order to ascertain this the following method was employed. A portion of the raw skin was suspended in sulphuric ether, in which some pieces of calcium chloride were placed. After the water of the skin had passed out, it was dried in a vacuum over sulphuric acid at 50°, and weighed. When tanned, this was found to increase 24·7 per cent. in weight: direct estimation of the amount of iron and sulphuric acid in the leather gave 26·4 per cent. The specimen taken was a piece of calf's skin. With thicker hides 100 parts by weight can take up 30, 40, 50, 60, to 80, and even 100 and 137 parts of tanning salt. Ludwig Kester, of Giesing, near Munich, has made experiments on vegetable tanning matters, and gives the following:—

Name.	Weight of 2 calf-skins, air dried.		Increase of weight during tanning.		Amount of Material used in Tanning.	
	Raw.	Finished.	Absolute.	Per cent.	2 hides.	1 part by weight of air-dried skin.
	g.	g.	g.		g.	pts. by wght.
Catechu	984	1435	451	45·8	2000	2·1
Pine bark	971	1450	479	49·3	18000	18·5
Old oak bark	973	1454	481	49·4	22500	23·1
Young „	972	1468	496	51·0	12000	12·3
Gall nuts	920	1430	510	55·4	1600	1·7
Dividivi	1005	1570	565	56·2	2000	2·1
Tormentil	1064	1699	635	59·7	9000	8·4
Mirobalans	998	1622	624	62·5	2000	2·1
Dohra-bark	952	1599	647	68·0	2000	2·1
Sumach	1016	1717	701	69·0	4500	4·4

Tanning by iron salt can, it will be seen from this table, give as good results, and present as little difficulty in this direction as the various substances detailed above.

The last point noticed was that the dressing which follows the tanning, having been made to suit the leather prepared by the aid of vegetable tans, was found not to give good results with iron-tanned leather. The statement of a judge of such matters was, "it gives weight, but a hard and crackly leather of no special value." This difficulty was overcome by treating the hide with fat and the so-called iron-soap after the tanning. Stearin and paraffin can be used for this purpose. The iron-soap is prepared by decomposing solutions of soap with the iron-salt previously mentioned. This iron-soap, with or without an addition of fat emulsion, is worked into the hide in a peculiarly constructed fulling-vat. S.

General and Physical Chemistry.

Variations in the Absorption Spectra of Colouring Matters. By — W. Vogel (*Deut. Chem. Ges. Ber.*, xi, 622—624).—The author gives accurate descriptions of the absorption spectra of naphthalene red, obtained by examining it under various conditions, viz., in the solid form, in alcoholic and aqueous solutions, and diffused through the substance of paper, shellac, and gelatin. The spectra obtained under these circumstances vary considerably. C. F. C.

Electrolysis with Evolution of Hydrogen at both Poles. By E. Elsässer (*Deut. Chem. Ges. Ber.*, xi, 587—590).—The author has repeated his experiments on electrolysis, in which magnesium was used as the anode, and hydrogen was evolved at both poles. He confirms his previous results (*Ber.*, ix, 1818), which were called in question by Beetz (*ibid.*, x, 118), and shows that the relation between the volume of hydrogen evolved at each pole is independent of the strength of the galvanic current, and, within certain limits, independent of the strength of the solution. W. C. W.

The Magnetic Behaviour of Chemical Compounds. By G. Wiedemann (*Phil. Mag.* [5], ix, 161—174, and 276—291).—The investigation of bodies by purely chemical or electrolytic methods necessarily involves a displacement or separation of atoms, so that it is only during or at the end of certain states of motion that it is possible to consider the manner in which the atoms were previously combined. The magnetic investigation of compounds, on the contrary, offers this advantage, that it is possible to study at least one physical property altogether characteristic of the individual atom, without any decomposition of the compound, and to draw conclusions respecting the behaviour of the atom, or constitution of the compound, which could never be deduced from the results obtained by either of the methods of investigation previously mentioned.

The method of operating was briefly as follows:—A long and heavily-loaded wire, forming part of an ordinary torsion balance, was fitted a little above its central point, with a horizontal arm, to the extremity of which was attached and counterpoised a light glass flask. In the latter was placed a solution of the substance whose magnetic moment was to be determined, and the whole system was so arranged as to be capable of being brought under the influence of a powerful electro-magnet, one of the poles of which was placed in a line with the centre of the flask. A mirror attached to the wire, and a scale at a distance of about 2 meters, were used as a means of determining the angle of torsion.

The zero position of the flask and its contents was first determined, without the magnet's influence; then the magnet was excited and its moment J determined by the oscillations of a magnetic needle arranged in the direction of its axis; the head of the torsion balance was then turned until the system was brought back to zero. On opening the magnetizing current, the apparatus rotated through a certain angle T, which was measured by means of the mirror and scale before mentioned. The value $M = \frac{T}{J^2}$ then measures the magnetic moment of the flask, and the contained substance for the unit moment of the magnet acting upon them.

Operating as above described, the following data were established:—

1. That within the limits of observation, the magnetic moment of the vessel filled with *ferrous sulphate* solution is directly proportional to the magnetising force acting upon it.

2. That the magnetism of salt solutions of different strengths is directly equivalent to the sum of the magnetisms of the solvent and the salt dissolved, and the magnetism of the latter is proportional to the weight contained in the unit of volume.

3. That the magnetism of the dissolved salt is nearly independent of the nature of the solvent.

4. That the magnetism of every salt in solution which has been examined diminishes proportionately with a rise of temperature, according to the equation $m = 100—0·325t$, the magnetism at 0° being supposed equal to 100.

Let m represent the magnetism calculated for the unit of weight of a salt dissolved in water, and let A represent its molecular weight, then $\mu = Am$ represents its molecular magnetism (μ). In a similar manner the atomic magnetism (α) may be calculated. It was found that the molecular magnetism of the dissolved haloïd and oxygen salts of the same metal with different acids was approximately the same, while the atomic magnetism of different metals varied, as shown below. If $\alpha = 100$ represents the iron in a *ferric* salt, we have:—

Ferric....	100·0	Cobalt ..	67·2	Nickel ..	30·5
Manganese	100·4	Chromic..	41·9	Cupric ..	10·8
Ferrous ..	83·1				

The magnetism of *solid* salts, combined with water of crystallisation, is approximately the same as that of the salts in solution, but on the salts being dehydrated, their magnetism is generally slightly reduced.

Double Decomposition.—On mixing solutions which mutually exchange their constituents, the total magnetism of the solutions is the same after as before the double decomposition; but it was noticed that in general the molecular magnetism changes if the constitution of the compounds change, as for instance, in the case of the cupric salts, which are strongly magnetic, whilst the cuprous salts and metallic copper are feebly diamagnetic.

An examination of the precipitated hydrates of several metals showed that their molecular magnetisms were approximately the same as those of the corresponding salts in aqueous solution. The magnetism of true colloidal solutions of the hydrates, however, was different, appearing to depend partly upon the nature of the solvent, and partly upon the possibility of the hydrate entering into chemical combination with any of the substances employed in its solution.

The anhydrous oxides of the magnetic metals exhibited a much feebler magnetism than their corresponding hydrates, but the results varied with the physical condition of the oxides. The dilution of ferric and chromic oxides, by precipitating them together with an indifferent oxide, such as alumina, and calcining the mixture afterwards, greatly increased the apparent magnetism of these substances; the magnetism of the iron oxide being quadrupled, and that of the chromium oxide nearly doubled.

The magnetism of the hydrated *peroxides* and *sulphides* of cobalt, nickel, and manganese is very small, whilst that of the chromium oxide or hydrate to which the formula CrO_2 is generally given is about equal to the atomic magnetism of chromium in the ordinary chromic salts; the change of colour from violet to green, produced in solutions of chromium compounds by subjecting them to prolonged heating, does not affect the magnetic character of these salts.

The *cyanides* of the magnetic metals possess in the hydrated condition a lower magnetism than the corresponding oxygen and haloïd salts, but this is often slightly increased on drying. Ferro- and ferri- cyanides, mangani-, and cobalti-cyanides, on the other hand, are almost destitute of magnetic power; the ferri-cyanides, indeed, are generally feebly diamagnetic, as also are some double cyanides, such as the double cyanide of nickel and potassium. The ammoniacal compounds of cobalt, nickel, chromium, and copper behave, as regards their magnetic deportment, much in the same manner as the ordinary salts of these metals; but the oxidised ammoniacal compounds of cobalt, such as the salts of purpureo-, roseo-, and luteo-cobalt exhibit either a very feeble magnetic moment, or are altogether diamagnetic in character. We must then assume that in the latter salts the cobalt is combined in quite a different manner from that in which it is in the ordinary cobaltic salts, or in those analogous to ferric salts. It is possible that, like the iron in the ferro-cyanides, the cobalt is combined in some feebly magnetic group, or perhaps that it replaces a portion of the hydrogen of the ammonium grouping.

It is known that many ferric salts in solution undergo dissociation by dilution only, at a lower or higher temperature into colloid ferric oxide and acid. It has been further shown that the magnetism of a unit weight of iron in the colloid ferric oxide is only 0·2198 of the magnetism of the oxide in combination with an acid; consequently, by the determination of the magnetism of these salts, their partial dissociation can be quantitatively verified. In this way it was ascertained that whilst in ferric chloride solutions dissociation proceeds slowly with increasing dilution, in neutral solutions of ferric sulphate about 25 per cent. of the salt is permanently dissociated, independently of the strength of the solution. The same results obtain in the case of iron-alum.

In solutions of ferric nitrate, 32 per cent. of the total iron was in the colloid condition, which increased to 36 on further dilution; with ferric acetate nearly 70 per cent.; and with ferric tartrate about 57 per cent. had dissociated.

From the foregoing experiments it is obvious that the magnetic moment of a solution may in some cases be made use of to measure the extent to which combination has taken place, when a molecule of any base is mixed with varying proportions of acid. Thus, by the gradual addition of sulphuric acid to 1 molecule of ferric hydrate, it was found that when as much as 1 molecule of acid had been added, 75 per cent. only had entered into combination, and that it was necessary to employ 4 molecules of sulphuric acid to 1 molecule of hydrate, in order to bring the whole of the latter into union with the acid. Similar results were obtained with ferric hydrate and nitric acid.

The author proposes to determine the alteration in magnetism of solutions of colloidal ferric hydrate and of ferric chloride, produced by variation of temperature, and to determine directly in this manner the influence of temperature upon dissociation; and further to bring, if possible, this method of experimenting to bear upon the determination of the mutual action of salts upon each other in aqueous solution.

J. W.

Combustion in the Eudiometer. By P. SCHÜTZENBERGER (*Compt. rend.*, lxxxvi, 600, 601).—In this paper the author examines the conditions under which the electric spark causes, or fails to cause, the combination of a mixture of oxygen and hydrogen gases in eudiometers of various lengths and diameters and under varying pressures.

R. R.

Thermo-Chemistry of Aluminium Compounds. By M. BERTHELOT (*Compt. rend.*, lxxxvi, 787—791).—The author has investigated the thermal relations of the oxide and halogen-compounds of this metal, by means of the following methods:—(1.) The heat of solution of the halogen-compound having been determined, an equivalent of ammonia was added to the aqueous solution, and the heat evolved during the reaction measured. From these data the difference between the heat of formation of the anhydrous halogen salt and of the precipitated oxide was determined. (2.) As an example: On the one hand, anhydrous Al_2Cl_6 was added to water holding in solution the equivalent quantity of KBr; on the other hand, Al_2Br_6 was added to a solution of the equivalent quantity of KCl. The difference between the quantities of heat evolved in the respective reactions is that between the heats of formation of the anhydrous salts. The following are the more important results of this investigation:—

The heat of formation of the hydrated oxide exceeds that of the anhydrous chloride by 34·9, the latter being 160·9 (Thomsen); the former is equal to 195·8. As the heat absorbed in the expulsion of water to form the anhydrous oxide may, without sensible error, be taken to be equal to that evolved in the molecular condensation attending its formation, this number represents the heat of formation of aluminium oxide. Thus, from the author's researches, we have:—

*$Al_2 + O_6$	evolves....	195·8 heat-units.
$Al_2 + Cl_6$	,, ...	160·9 ,,
$Al_2 + Br_6$ (vapour)	,, ...	132·6 ,,
$Al_2 + I_6$,,	,, ...	86·3 ,,

The considerable differences observed between the heats of formation of the iodide and bromide on the one hand, and the oxide on the other, explain the ignition of the former compounds when heated in an atmosphere of oxygen.

C. F. C.

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* $O = 8$.

Expansion of the Solid Elements by Heat, a Function of the Atomic Weight. By H. F. WIEBE (*Deut. Chem. Ges. Ber.*, xi, 610—612).—The author has compiled and tabulated existing data respecting the expansion of the solid elements by heat, and considers that he has obtained sufficient evidence to warrant the conclusion that the absolute expansion of the atoms is a periodic function of their atomic weight. In the following table, which expresses the numerical bases of this deduction, columns II and III give the densities and atomic weights of the elements; column IV contains the coefficients of expansion in 100,000,000 parts at 40°; column V the relation of this coefficient to the quotient of III by II for each element.

I.	II.	III.	IV.	V.
Al......	2·56	27·3	2313	247
Si......	2·49	28·0	763	86
S.......	2·04	31·98	6413	1005
Fe......	7·8	55·9	1188	85
Co......	8·5	58·6	1236	85
Ni......	8·8	58·6	279	85
Cu	8·8	63·3	1684	121
Zn	7·15	64·9	2918	265
As......	5·67	74·9	559	64
Se......	4·6	78·0	3680	624
Ru	11·3	103·5	963	88
Rh	12·1	104·1	850	73
Pd	11·5	106·2	1176	109
Ag	10·5	107·66	1912	197
Cd	8·65	111·6	3069	396
In......	7·42	113·4	4170	637
Sn......	7·29	117·8	2234	361
Sb......	6·7	122·0	1152	210
Te......	6·25	128·0	1675	343
Os......	21·4	198·6	657	61
Ir......	21·15	196·7	700	65
Pt	21·15	196·7	899	84
Au	19·3	196·2	1443	147
Tl......	11·86	203·6	3021	519
Pb......	11·83	206·4	2924	510
Bi......	9·82	210·0	1346	288

The numbers in column V exhibit certain interesting relations between the numbers of natural groups of the elements, *e.g.*, As : Sb : Bi = 1 : 3 : 4 and Zn : Cd = 2 : 3. Represented graphically, they give a curve similar to that of atomic volumes. C. F. C.

Tension of the Vapour given off by a Mixture of two Liquids. By E. DUCLAUX (*Compt. rend.*, lxxxvi, 592—594).—Aqueous solutions of monatomic alcohols when distilled follow the law, $\frac{\alpha}{\epsilon} = m\frac{a}{a+e}$, in which a and e represent the volumes of alcohol and of water in the liquid heated, and α and ϵ the volumes of those substances in the distillate. The coefficient m increases with the molecular weight of the alcohol. Aqueous solutions of acids of the fatty series treated in like manner follow the law $\frac{a}{\epsilon} = m \frac{a}{e'}$, the coefficient m increasing as we ascend in the series of fatty acids.

From these ratios of the quantities of the liquids distilled over, the ratios of the volumes of vapours may be deduced. This for the alcohols is $\frac{A}{E} = p \frac{a}{a + e'}$, and for the acids $\frac{A}{E} = p \frac{a}{e_1}$. The value of p is the same for methylic, ethylic, and propylic alcohols; the same also for butylic, amylic, and caprylic alcohols; and again the same for formic and acetic acids. From which it appears that in each of these groups, the volumetric composition of the vapour which escapes from a liquid of given composition is independent of the nature of the body which enters into the mixture. The different value of p in the two alcohol groups appears to depend upon the different solubilities of the substances in water.

From the ratio $\frac{A}{E}$ the ratio of the tensions $\frac{f}{f_1}$ can be deduced, and since their sum is known each can be calculated. It can thus be shown that the vapour of alcohol is never saturated, that its tension increases with the proportion of alcohol present in the mixture, and that for alcohols of the same group it is constant for liquids of like composition. It is found moreover that the aqueous vapour is always almost completely saturated, the saturation being more complete the less soluble the alcohol is in water. These laws permit the boiling point of mixtures of known composition to be in many cases calculated beforehand, being that at which the tension of the aqueous vapour given off is at its maximum.

The tendency which alcohol vapour, as stated above, has to predominate is counteracted by that of aqueous vapour to remain saturated, so that at a certain stage, a state of equilibrium is established, the vapour which is given off has a tolerably constant composition, and the boiling point also remains nearly constant. R. R.

Concussion-figures of Galena and Corrosion-figures of Gypsum.

By E. Weiss (*Jahrb. Min.*, 1877, 831—833).—When the point of a steel needle is placed on the fresh smooth surface of a thick piece of galena, and the needle is struck with a gentle blow, fine smooth streaks or cracks, which are bounded by a glimmering sheen of light, are seen to run parallel to the edges of the cube from the point of concussion to 1, 2, 3, or 4 sides. When examined by reflected light under a magnifier it is seen that this sheen is caused by fine closely crowded laminæ, which form brilliant lines on both sides of the streak not quite perpendicular to its direction, but directed at very obtuse angles outwards. The explanation is that a slight dislocation of the mass makes itself felt in the four directions parallel to the axes. In the breadth of the streak the little particles remain parallel and the surface reflects light as before, but at the sides a slight turning of the laminæ takes place and hence the sheen. This phenomenon does not occur in every specimen of galena.

When a plate of gypsum is cemented by Canada-balsam to a glass plate and gently heated (but not for too long a time), the clouded part which is produced is much broken up, and between the gaps and at the edges large quantities of little isolated points appear, which form a design resembling an envelope. Four branches run almost from the same point, of which those which run to opposite sides are parallel. They do not cut at right angles, but at an angle however of more than 80°. The whole design is surrounded by a border produced by the union of the ends of the upper branches, so that a kind of square is formed in which the whole design is contained, and in which the four branches are diagonal and form four triangular spaces. Of these spaces, two opposite ones are brighter and two darker, and this is due to two systems of streaks which run through the spaces. The lines which produce the streaks are not quite sharp, straight, and uninterrupted, but they run in definite directions. In the brighter spaces there is only one system of fine lines; in the darker spaces there are two systems, a fine one running back and a coarser one cutting the main branch at about 25°. The first line-system runs parallel with the orthopinacoïd, the second forms with it an angle of about 66°. G. T. A.

Inorganic Chemistry.

On Deacon's Chlorine Process. By C. HENSGEN (*Dingl. polyt. J.*, ccxxvii, 369—374).—In a previous paper (this *Journal*, 1877, i, 439) the author has stated that the action of dry gaseous hydrochloric acid on anhydrous copper sulphate, at the ordinary temperature, forms a compound which no doubt plays an important part in the production of chlorine by Deacon's process. It is now found, from the quantity of free chlorine and water obtained, that the reaction which ensues when this body is heated at a temperature of 300—400° in a stream of dry air or oxygen may be expressed by the equation

$$CuCl_2 + H_2SO_4 + O = CuSO_4 + H_2O + Cl_2.$$

The anhydrous copper sulphate in a stream of dry gaseous hydrochloric acid gas is converted into $CuCl_2 + H_2SO_4$, a compound which is at once split up by oxygen and heat; at the same time the disengaged hydrochloric acid is decomposed into free chlorine and water.

If there be more sulphuric acid present than is expressed by $CuCl_2 + H_2SO_4$, it was found that there is a decrease in the production of chlorine, owing to the hydrochloric acid gas being disengaged more rapidly than it can be acted on by the oxygen. This result explains what has been observed in Deacon's process, when, after some time, there is a decrease in the quantity of chlorine from the accumulation of free sulphuric acid in the clay material which has been saturated with copper sulphate.

Wislicenus (*Jahresbericht*, 1873, 1012) has explained the reaction which takes place in Deacon's process by assuming it to occur between the hydrochloric acid gas and the water in a sulphate of the composition of $CuSO_4,H_2O$; but the author has endeavoured to show that the formation of chlorine is possible without the presence of water. As copper sulphate becomes anhydrous at 240°, it is very doubtful whether water could still take part in the reaction at the higher temperature of 300—400°.

Copper chloride in a finely-divided condition, when subjected to the action of dry gaseous hydrochloric acid and oxygen, gives a considerable quantity of free chlorine, and at a lower temperature than is required by heat alone. In three series of experiments, by using clay-balls which had been saturated with copper chloride and cautiously dried, and employing a temperature of 100°, 200°, and 300° respectively, it was found that the variation in temperature does not affect the production of chlorine, which takes place according to the equations:—

$$(1.)\ 2CuCl_2 = Cu_2Cl_2 + Cl_2.$$
$$(2.)\ Cu_2Cl_2 + 2HCl + O = 2CuCl_2 + H_2O.$$

It is possible, however, that an intermediate oxychloride is formed, thus:—

$$Cu_2Cl_2 + O = CuO.CuCl_2, \text{ then } CuO.CuCl_2 + 2HCl = 2CuCl_2 + H_2O.$$

A. J. C.

Atmospheric Hydrogen Peroxide. By E. Schöne (*Deut. Chem. Ges. Ber.*, xi, 482—492).—The rain, hail, sleet, and snow which fell in Moscow from July 1st, 1874 to June 30th, 1875, were carefully tested for hydrogen peroxide, and the results of the examination are tabulated so as to show the influence of the direction of the wind and of the time of the year on the quantity of hydrogen peroxide contained in the rain, &c. Hydrogen peroxide was detected with certainty in 208 of the 215 specimens of hail and rain, and in 86 of the 172 samples of snow and sleet which fell during the year.

The rain or snow generally contains more hydrogen peroxide when the centre of maximum barometric depression lies north of Moscow than when it lies to the south; and under similar conditions the quantity of hydrogen peroxide increases as the centre of depression approaches the meridian of Moscow on the north side, and diminishes as it draws nearer the meridian on the south side.

Hydrogen peroxide is most plentiful in July and least abundant in December and January. Struve's statement (*Zeitschr. f. Anal. Chem.*, viii, 320) that snow contains more hydrogen peroxide than rain is contrary to the author's experience.

W. C. W.

Atmospheric Hydrogen Peroxide. By E. Schöne (*Deut. Chem. Ges. Ber.*, xi, 561—566).—The quantity of hydrogen peroxide in the atmosphere, at different hours of the day and during different seasons of the year, was estimated by producing dew or hoar frost artificially and measuring the amount of hydrogen peroxide it contained. The experiments could not be successfully continued during January, February, and March, on account of the dryness of the atmosphere at Moscow at this time of the year. The following results were obtained:—

	Number of experiments.	Mgms. H_2O_2 in 1 litre of dew or hoar frost.	c.c. H_2O_2 vapour in 1000 c.c. of air.
July, 1874	29	0·144	0·389
August, 1874.......	20	0·105	0·364
September, 1874 ..	7	0·071	—
October, 1874.......	8	0·056	—
December, 1874....	1	0·045	—
March, 1875	2	0·055	—
June, 1875........	22	0·128	0·317
July, 1875	49	0·137	0·396

The atmosphere contains the minimum amount of hydrogen peroxide between midnight and 4 A.M. and the maximum quantity at 4 P.M. The air in an unused room contained 0·17 c.c. H_2O_2 per litre, but no hydrogen peroxide could be detected in the atmosphere of a badly ventilated dwelling room. W. C. W.

Dilatation of Fused Sulphur. By S. SCICHILONE (*Gazzetta chimica italiana*, vii, 501—505).—This is a continuation of Pisati's researches already published (*Gaz.*, vii, 337, and this *Journal*, 268). The author finds that sulphur precipitated from sodium thiosulphate and repeatedly crystallised possesses the same coefficient of expansion as natural crystals of sulphur, the numbers expressing the specific volumes of the two kinds differing only in the fourth decimal place. The same sulphur, after being exposed to a temperature of 250° for two days, is somewhat changed; for although the minimum remains at about 159°, the specific volume is somewhat greater at all temperatures below 220°. The same sulphur, after being boiled, gave results for the coefficient of expansion almost identical with those obtained by Moitessier; the author gives the minimum at about 162°, however, instead of 165° (Pisati). C. E. G.

Sulphur Chloride. By ISAMBERT (*Compt. rend.*, lxxxvi, 664—665).—In order to ascertain whether a higher chloride of sulphur is formed or not when chlorine is absorbed by sulphur chloride, SCl_2, the author has determined the tension of the chlorine in solution, at temperatures between 4° and 10°, which he finds to vary constantly with the amount of chlorine dissolved, and he therefore concludes that the chlorine is merely held in solution and does not enter into combination.* L. T. O'S.

The Boiling Points of Sulphuric Acid of Different Concentration. By G. LUNGE (*Deut. Chem. Ges. Ber.*, xi, 370—374).—The only table hitherto constructed to show the boiling points of sulphuric acids of different concentration is that of Dalton in his "New System of Chemistry," but as his results are to some extent inaccurate, the author has redetermined these constants. About 150 c.c. of the acid were heated to boiling in a flask with a long neck, so that the volatilised acid might flow back into the vessel. A thermometer was suspended in the neck of the flask, so that the bulb was completely under the surface of the liquid, in which a spiral of platinum wire was placed in order to avoid tumultuous boiling. That was taken as the boiling point at which the whole column of mercury became completely immersed in the transparent vapour. The following table represents the results obtained, which, with the exception of the lower ones, are considerably higher than those got by Dalton :—

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* The author appears to be unacquainted with the researches of Michaelis (*Liebig's Annalen*, clxx, 6).—C. E. G.

Observed Volume Weight.	Temperature.	Volume Weight reduced to 15° C.	Corresponding p. c. of H_2SO_4.	Observed b.-p.	Barometer reduced to 0°C.
1·8380	17	1·8400	95·3	297	718·8
1·8325	16·5	1·8334	92·8	280	723·9
1·8240	15·5	1·8245	90·4	264	720·6
1·8130	16	1·8140	88·7	257	726·0
1·7985	15·5	1·7990	86·6	241·5	720·1
1·7800	15	1·7800	84·3	228	720·5
1·7545	16	1·7554	81·8	218	726·0
1·7400	15	1·7400	80·6	209	720·6
1·7185	17	1·7203	78·9	203·5	725·9
1·7010	18	1·7037	77·5	197	725·2
1·6750	19	1·6786	75·3	185·5	725·2
1·6590	16	1·6599	73·9	180	725·2
1·6310	17	1·6328	71·5	173	725·2
1·6055	17	1·6072	69·5	169	730·1
1·5825	15	1·5825	67·2	160	728·8
1·5600	17	1·5617	65·4	158·5	730·1
1·5420	17	1·5437	64·3	151·5	730·1
1·4935	18	1·4960	59·4	143	730·1
1·4620	17	1·4635	56·4	133	730·1
1·4000	17	1·4015	50·3	124	730·1
1·3540	17	1·3554	45·3	118·5	730·1
1·3180	17	1·3194	41·5	115	730·1
1·2620	17	1·2633	34·7	110	732·9
1·2030	17	1·2042	27·6	107	732·9
1·1120	17	1·1128	15·8	103·5	732·9
1·0575	17	1·0580	8·5	101·5	735·0

A curve, differing very little from a parabola, is obtained by taking the percentage amounts of H_2SO_4 as abscissæ and the corresponding boiling points as ordinates. T. C.

The Chemical Reactions of the Electric Spark in the Formation of Persulphuric Oxide. By Berthelot (*Compt. rend.*, lxxxvi, 277—279).—The author, with the view of preparing persulphuric oxide directly from oxygen and sulphur trioxide, passed the electric spark at a high tension through a mixture of the two bodies for some time. The gas in the tube diminished from 60 c.c. to 40 c.c., and the sulphur trioxide was replaced by a body resembling the persulphuric oxide prepared from sulphur dioxide, and which on examination was found to have the same composition, S_2O_7. Persulphuric oxide decomposes slowly when kept, yielding either sulphur trioxide or a mixture of that body with some undecomposed acid. Like ozone and hydrogen dioxide, persulphuric oxide decomposes by degrees when the external energy under the influence by which it is formed, ceases.

In the formation of persulphuric oxide, an excess of oxygen is necessary, otherwise the reaction is incomplete, which fact, according to the author, gives evidence in support of the double action exerted by the electric spark, which is capable of decomposing binary compounds into their elements, and recombining them to form more complex substances, until equilibrium between the decomposition into simple and the formation of the complex compounds is established. Similar effects have been observed in the action of heat and light on bodies. The equilibrium which attends these syntheses may be explained as the result of the opposition of the two energies (chemical and calorific) the former of which causes the disengagement of large quantities of heat, and the latter (luminous or electric) being accompanied by the absorption of heat. L. T. O'S.

Reaction of Boric Acid in presence of Mannite. By D. KLEIN (*Bull. Soc. Chim.* [2], xxxix, 178—196).—If a solution of boric acid, so dilute as not to affect blue litmus, is added to a concentrated solution of mannite, the mixture acts on blue litmus immediately. This reaction is so delicate that when 5 c.c. of a solution of boric acid containing 1 in 100,000 are added to 5 c.c. of a 15 per cent. mannite solution, the mixture turns blue litmus red after the lapse of 1 minute; this is the limit of the reaction. The author gives a table showing the sensibility of the reaction. L. T. O'S.

On the Amount of Carbon Dioxide in Ground-air. By P. SMOLENSKY (*Zeitschr. f. Biologie*, xiii, 383—394).—The literature of the subject consists of papers:—

(1.) By M. v. Pettenkofer (*Zeitschr. f. Biologie*, vols. vii, ix, xii).

(2.) By H. Fleck (*Jahresber. d. Chem. Centralstelle f. öffentliche Gesundheitspflege in Dresden.*

(3.) By J. v. Fodor (*Vierteljahresschrift f. öffentl. Gesundheitspflege*, vol. vii, 1875).

(4.) By Lewis and Cunningham (Ditto, vol. viii, 1876).

(5.) By Nicholls (Ditto, ditto).

The method adopted by the author was to drive iron tubes, provided with a side opening, about two meters deep into the ground, and then to suck out the air till the tubes were full of ground-air, and determine the amount of carbon dioxide. The conclusions drawn from the experiments are, that the great importance attributed by Fleck, and particularly by v. Fodor, to the permeability of the ground in question is open to great doubt: that v. Fodor's experiments are not sufficient to show that the ground was less impure where a greater quantity of carbon dioxide was found: that it is very doubtful whether the "lively" motion of the ground-air spoken of by v. Fodor has any existence. G. T. A.

Analysis of Glass. By S. KERN (*Chem. News*, xxxvii, 183).—A gauge-glass fitted to a boiler was analysed, as it had been found to be corroded to a great extent:—

	SiO_2.	CaO.	Na_2O.	Al_2O_3 Fe_2O_3.	H_2SO_4.	
Upper part....	72·65	9·94	15·10	2·18	0·01	= 99·88
Lower part....	72·62	9·96	15·42	1·98	traces	= 99·98

D. B.

Gallium. By LECOQ DE BOISBAUDRAN and E. JUNGFLEISCH (*Compt. rend.*, lxxxvi, 577—579).—By introducing into fused gallium, cooled down a few degrees below its melting point, a piece of platinum wire to which a fragment of solid gallium is attached, octohedral crystals of the metal may be obtained. Gallium is hard and but little malleable; it spreads under the hammer, and acquires the polish of the anvil, but it soon becomes brittle and splits at the edges. In small bars it exhibits a remarkable degree of solidity, even at a temperature approaching its melting point. In thin plates it can be bent several times at a sharp angle without breaking. In spite of its hardness, gallium leaves on paper bluish-grey traces. It preserves its lustre in the air, even of a laboratory, and in water free from air, but in ordinary water it slowly tarnishes. In the fused state the metal has the colour of tin or silver; but light reflected several times between two polished surfaces exhibits a bluish-green colour. Chlorine powerfully attacks gallium in the cold; the product is crystalline and nearly colourless, having a tinge of yellow, probably due to some impurity; it is very fusible; volatilises easily and absorbs moisture from the air. Bromine has a less energetic action, and the combination with iodine is effected by the application of a gentle heat. The bromide and iodide resemble the chloride in their general properties. R. R.

Specific Heat and Heat of Fusion of Gallium. By BERTHELOT (*Compt. rend.*, lxxxvi, 786—787).—The author has determined the specific heat of the solid metal, between 12° and 23°, to be 0·079. The product of this number into 69·9, the atomic weight of the metal as determined by Boisbaudran, gives the number 5·52 as expressing its atomic heat.

The specific heat of the liquid metal, between 119° and 106°, is 0·0802 (atomic heat = 5·59), and differs, therefore, but slightly from that of the solid: in this respect it resembles mercury, lead, bismuth, and other metals.

The heat of fusion of gallium, referred to its atomic weight, is 1·33 (cal.). C. F. C.

Specific Heat of Glucinum. By L. F. NILSON and O. PETTERSSON (*Deut. Chem. Ges. Ber.*, xi, 381—386; also *Compt. rend.*, lxxxvi, 823—826).—Our present knowledge of the glucinum compounds does not allow us to say positively whether the oxide is G_2O_3 or GO. The authors have endeavoured to decide this by a determination of the specific heat of the metal. Quite recently Emmerson Reynolds determined the specific heat of glucinum, and obtained a number agreeing with the atomic weight 9·4, showing that glucinum is a dyad. The authors, however, have come to a different conclusion. They, like Reynolds, prepared their glucinum by the action of sodium on the chloride, but used a strong iron cylinder closed with a screw, and not glass, porcelain, or platinum vessels, as the latter are strongly attacked, whilst the resulting glucinum is largely contaminated with silicon, aluminium, &c.

The metallic glucinum obtained by the authors consisted of microscopic and sometimes larger prismatic crystals of the colour and lustre of steel. The metal is unaltered in the air, and does not decompose water; in dilute acids or caustic alkalis it dissolves, with evolution of hydrogen. Oxygen or sulphur does not attack it, even at a red heat, but it burns when heated in chlorine. Its sp. gr. at 9° C. is 1·9101. An analysis of the metal gave SiO_2, 0·99; Fe, 2·08; oxide of glucinum, 9·84; G, 87·09 = 100. From this, the density of silica, iron, and glucina being known, the sp. gr. of the pure metal may be calculated; this is 1·64.

The specific heat of the impure metal was determined with Bunsen's ice calorimeter, and corrections were made for the iron, silica, and oxide of glucinum present, the specific heat of the latter having been found to be 0·2471 at 0—100° C. In this way the specific heat of the pure metal was found to be 0·4079 at 0—100° C., so that the atomic weight of glucinum is 13·8 and not 9·2, as usually taken, and consequently the formula of the oxide is G_2O_3. This places glucinum in the aluminium rather than in the magnesium group of elements. T. C.

Atomic Weight of Glucinum. By L. Meyer (*Deut. Chem. Ges. Ber.*, xi, 576—579).—The author considers it probable that if glucinum is trivalent (according to the determination of the specific heat by Nilson and Pettersson), its atomic weight will be 11—11·5 instead of 13·8, and the metal will occupy a position between boron and carbon in Mendelejeff's table, and will be the first member of the aluminium group of elements. If the atomic heat of oxygen is calculated from the difference between the atomic heat of glucinum and the molecular heat of its oxide, it will be found to be 2·5 instead of 3·5—5·1. This circumstance favours the supposition that the determination of the specific heat of glucinum by Reynolds is more correct than the experiments of Nilson and Pettersson. W. C. W.

Allotropic Varieties of Magnetic Oxide of Iron. By H. Moissan (*Compt. rend.*, lxxxvi, 600).—Magnetic oxide of iron, obtained by heating its peroxide for some hours in hydrogen gas or carbonic oxide at 350—440°, or by heating the hydrate of the magnetic oxide at 300° in an indifferent gas, or by calcining the pyrophoric protoxide at a low red heat, passes into peroxide by calcination in the air, and is attacked by concentrated nitric acid. Its density is 4·86. Magnetic oxide obtained at a high temperature by burning iron in oxygen, or by decomposing the sesquioxide at a bright red heat, has a density of 5 to 5·09, and does not possess those properties. Pyrophoric protoxide of iron is transformed when heated in the air into peroxide, but if this substance be heated to dull redness in carbonic acid gas, magnetic oxide is obtained identical with the first variety mentioned above. If this variety be heated intensely in nitrogen, the second kind, namely, that incapable of taking up more oxygen, is the product. R. R.

A Manganese Blue. By G. BONG (*Bull. Soc. Chim.* [2], xxix, 199—201).—By fusing any manganese compound (free from iron) with silica and baryta or a mixture of soda and lime, a blue compound is obtained, the intensity of the colour of which depends on the quantity of manganese used, but it may be changed to green or violet by adding different quantities of alkali or silica. The blue compound, which appears to be a silico-manganate of the alkaline earths, is destroyed by reducing agents, acids, and after some time by water, but resists a temperature of 1100°. By means of this reaction the author proposes to detect traces of manganese in minerals. L. T. O'S.

Mineralogical Chemistry.

Molybdenite from Biella. By A COSSA (*Gazzetta chimica italiana*, vii, 505—508).—This specimen was found at Machetto, in Biella, disseminated in milky quartz, and associated with pyrites and a molybdenous ochre. It forms flexible plates, resembling graphite in colour, lustre, and hardness; sp gr. 4·704. The analytical results correspond with the formula MoS_2, which requires Mo = 59, S = 41. The mineral is not attacked by hydrochloric acid, but dissolves in nitric acid and in aqua regia. Pure boiling sulphuric acid attacks it but very slightly, which is contrary to the statement sometimes made, that the mineral is soluble in the boiling acid with a blue colour; it is only when organic matter or some reducing agent is present that this takes place. Placed in a solution of auric chloride at the ordinary temperature, the mineral soon becomes covered with a film of metallic gold, whilst molybdenum passes into solution. C. E. G.

Chrome Ore in New Caledonia. (*Dingl. polyt. J.*, ccxxvii, 507—508; *Metallurgical Review*, 1877, i, 300.)—Large quantities of a peculiar chrome ore have been found in New Caledonia. It consists of a hydrated oxide of iron containing chromium in a condition soluble in acids. Variety A has a reddish-brown colour and cellular structure; the cells are filled with a brown earthy mass, in which the chromium appears to have been concentrated. Variety B has fewer and smaller cells.

	A.	B.
SiO_2 and TiO_2	5·60	7·60
Al_2O_3	trace	trace
Fe_2O_3	69·60	73·00
Mn_3O_4	2·00	0·60
Cr_2O_3	5·33	2·85
MgO	trace	trace
CaO	trace	trace
P	not determined	
NaCl	trace	0·40
Loss on ignition	16·60	14·30
SO_3	0·60	0·70
	99·73	99·45

A, by dry assay gave a white button, amounting to 56·7 per cent., and containing 0·6 per cent. of chromium. B gave 59·85 per cent. of a white and very hard iron, containing 3·8 per cent. of chromium.

J. T.

Japanese Porcelain Earth. By C. W. Gümbel (*Dingl. polyt. J.*, ccxxvii, 500—502).—Near Arita, in the province of Hizen, are found the finest materials, which only require grinding and washing to serve for the production of the so-called egg-shell porcelain. Some specimens of the material employed were white, or faintly yellow, rather stony than earthy, compact, not porous, apparently uniform in composition, and without perceptible disseminated minerals. Only one sample was soft and earthy. The stony samples under the microscope showed a clear body with a large quantity of fine scattered particles, minute grains, and irregular splinters, perhaps of quartz, felspar, or mica. Most of the samples contained small crystals of pyrites. The earthy variety is only used in admixture with the stony varieties. The following results were obtained on analysis :—

	A.	I.	II.	III.	IV.	V.	VI.
SiO_2	75·9	70·74	77·35	83·00	80·00	79·73	49·25
Al_2O_3	20·0	21·75	14·27	11·60	12·00	12·45	38·89
Fe_2O_3	—	2·02	2·11	0·70	0·50	0·67	1·14
MnO	—	—	trace	trace	trace	trace	—
CaO	0·6	0·72	0·15	—	0·03	0·61	0·15
MgO		0·02	0·29	0·18	0·25	0·14	0·36
K_2O	3·5	3·23	1·78	1·90	2·40	1·71	2·01
NaO		2·43	0·32	0·09	0·57	0·27	0·39
Ti, S, &c.	—	—	1·09	trace	0·60	0·38	0·65
H_2O	—	—	2·76	2·43	3·00	2·24	5·90
	100·00	100·91	100·12	100·60	99·15	98·20	98·74

A. Sample analysed by Malaguti at Sèvres.
I. Good Japanese white porcelain.
II. Porcelain-stone with pyrites particles.
III. „ somewhat yellower.
IV. „ shining white.
V. „ containing pyrites.
VI. Shining white porcelain earth, similar to European porcelain clay, but containing less water.

On comparing the analysis of the raw material with that of the finished porcelain, it is evident that the porcelain mixture could be produced by taking about 2 parts of the stone with 1 part of No. VI together with perhaps a little felspar; or, as in China, a little lime and ash of some plant might be added.

J. T.

A New Mineral Spring near Pelm in the Kyllthal (Eifel). By H. Vohl (*Deut. Chem. Ges. Ber.*, xi, 605).—This spring contains the following substances: lime, magnesia, alumina, lithia, potash, soda, manganese, and ferrous salts, also carbonic, sulphuric, silicic, and phosphoric acids, chlorine, bromine, and iodine, and traces of baryta, strontia, and of boric acid. The water is very rich in iron, which soon separates out. W. C. W.

The Mineral Water of Challes, in Savoy. By E. WILLM (*Compt. rend.*, lxxxvi, 613—616).—There are two springs of this water; the one, known as the "petite source," contains less sulphur and iodine than the "source principale." They each give about 3,000 litres per day. Challes water when first collected is clear and free from colour and smell, although it contains much sulphur. When boiled, it gives off large quantities of sulphuretted hydrogen as a decomposition-product from the action of bicarbonates upon alkaline sulphides, or acid sulphides. This evolution of sulphuretted hydrogen is very rapid at the commencement, owing to the decomposition of bicarbonates of calcium and magnesium, but after a short time it takes place less quickly, as the sodium bicarbonate contained in the water gives off its carbonic acid more slowly.

The whole of the sulphur was found to be present in the form of sulphydrates (with the exception of sulphates); it was estimated by adding an excess of manganese sulphate to the water, and then boiling, when half the SH_2 combined with manganese, the other half going off in the form of gas. The boiling was continued until the evolution of CO_2 and SH_2 ceased; then the mixture was treated, with proper precautions, with hydrochloric acid, again boiled, and the gases were conducted through tubes containing arsenious acid dissolved in hydrochloric acid. The sulphide of arsenic thus obtained was collected and weighed. The sulphur was found to equal ·1058 per litre. An estimation of the total sulphur gave ·2127 per litre. (·1058 × 2 = ·2116).

On boiling, magnesium and calcium carbonates are precipitated, whilst sodium carbonate (or bicarbonate) remains in solution. The presence of potassium is doubtful. Lithium has been detected with the spectroscope.

The following is the composition of the water (temperature 10·5°):—

		Source principale.		Petite source.	
		Grams per litre.			
	Sulphur (sulphydrates)	0·2127		0·00337	
	Carbonic acid........	0·0674		—	
	Nitrogen	24·3 c.c.		—	
Deposit on boiling	Calcium carbonate....	0·0772	·1268	0·1325	·1531
	Magnesium carbonate..	0·0496		0·0206	
		Soluble salts.			
	Sand...............	0·0227		0·0232	
	Alumina	0·0059			
	Sodium sulphydrate ..	0·3594		0·0059	
	„ carbonate.....	0·5952		0·1146	
	„ sulphate	0·0638		0·1557	
	„ chloride......	0·1554		0·0232	
	„ bromide	0·00376		—	
	„ iodide........	0·01235		0·0080	
		1·21851		0·3306	

Challes water may be kept for long periods in well-corked bottles, without any change taking place. By exposure to the air for some time hyposulphites are finally formed, together with a deposit of sulphur. R. C. W.

Analysis of the Sulphureous Mineral Waters of Aix in Savoy, and of Marlioz. By E. WILLM (*Compt. rend.*, lxxxvi, 543—546).—The following results are given as the composition of the so-called "sulphureous" and "alum" springs at Aix, and of the waters of Marlioz, which is situated at a distance of one kilometre from Aix.

Aix Waters.

	"Sulphur" Water.	"Alum" Water.
Temperature	43·5 degrees.	44·6 degrees.
	Per litre.	Per litre.
Free sulphuretted hydrogen	3·37 mgrs.	3·74 mgr.
Sulphur in hyposulphites	3·84 "	3·60 "
Nitrogen gas	13·03 c. c.	12·5 c.c.
Carbonic acid gas	47·15 "	44·59 "
Deposit produced by Ebullition.		
Calcium carbonate	0·1894 grams	0·1623 grams
Magnesium "	0·0105 "	0·0176 "
Ferrous "	0·0010 "	0·0008 "
Silica	—	0·0175 "
Fixed Substances.		
Silica	0·0479 "	0·0365 "
Chlorine	0·0179 "	0·0166 "
SO_4	0·1503 "	0·1313 "
PO_4	0·0040 "	traces
Calcium	0·0280 "	0·0298 "
Magnesium	0·0167 "	0·0104 "
Sodium	0·0227 "	0·0284 "
Aluminium	0·0013 "	0·00005 "
Lithium	traces	traces
Potassium and strontium	?	?

Marlioz Water.

Temperature 11 degrees.

Deposit produced by Ebullition.

	Per litre.
Calcium carbonate	0·1912 grams
Magnesium "	0·0011 "

Fixed Substances in Marlioz Water.

Sodium sulphite	0·0285 grams
„ sulphate	0·2631
Calcium sulphate	0·0605
Magnesium chloride	0·0640
Sodium iodide	0·0015
Silica and alumina	0·0284

R. R.

Organic Chemistry.

Preparation of Methyl-Allyl. By H. GROSHEINTZ (*Bull. Soc. Chim.* [2], xxxix, 201—203).—By the action of zinc-methyl on allyl iodide, Wurtz (*ibid.*, 1867, viii, 265) obtained a butylene, which he called methyl-allyl. On repeating these experiments, however, the author has obtained a mixture of three isomeric butylenes, the bromides of which boil at 158°, 148°, and 168° respectively. The hydrocarbon whose bromide boils at 158° is formed in the largest quantity, whilst methyl-allyl, which ought to be identical with Wurtz's ethyl-vinyl, and whose bromide boils at 168°, is formed only in small quantities.* The bromide boiling at 148° is isobutylene bromide. In this reaction a molecular change takes place, by which methyl-allyl is converted into an isomeric butylene. The author has also observed a fourth bromide, which is very stable, and distils at 175—195°; it appears to be allyl tribromide, but is obtained in such small quantities that it has not been completely investigated. L. T. O'S.

Oxidation of the Valerylene $(CH_3)_2CH.C{\equiv}CH$. By FLAVITZKY and KRILOFF (*Bull. Soc. Chim.* [2], xxxix, 214).—By the oxidation of this valerylene, acetone, acetic acid and isolactic acid have been obtained, the hydrocarbon being split up at the triple linking. By the action of sulphuric acid, sp. gr. 1·65, the same valerylene yielded, amongst other products not yet studied, a ketone having the constitution, $(CH_3)_2CH.CO.CH_3$. L. T. O'S.

Tetramethylethene. By A. PAWLOW (*Deut. Chem. Ges. Ber.*, xi, 513).—Tetramethylethene (b. p. 73°) obtained by the action of alcoholic potash on dimethylisopropylcarbinyl iodide, unites directly with bromine, forming a solid compound, $C_6H_{12}Br_2$, which is soluble in ether, alcohol, and benzene. The ethereal solution deposits long, needle-shaped crystals, which melt with partial decomposition at 140°. $C_6H_{12}.HI$ boils at 140°, and solidifies at $-22°$. $C_6H_{12}.HCl$ boils at 112°, and solidifies at $-14°$. Tetramethylethene is completely oxidised to acetone by a 10 per cent. chromic acid solution; it is converted into dihexylene by the action of sulphuric acid at 60°.

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* Methyl-allyl and ethyl-vinyl are not identical, inasmuch as the boiling-points of their dibromides differ, according to Wurtz (*Bull. Soc. Chem.* [2], viii, 265), by about 10 degrees. Methyl-allyl, obtained by the action of zinc-methyl on allyl iodide, forms a dibromide boiling at 156—159°; ethyl-vinyl, obtained by the action of zinc-ethyl on vinyl bromide, boils at 165—166°. The two hydrocarbons are represented by the following constitutional formulæ:—

$CH_3—CH{=}CH—CH_3$. Methyl-allyl.

$CH_3—CH_2—CH{=}CH_2$ Ethyl-vinyl.

H. W.

The author considers it probable that pinacone is tetramethylethene glycol, since pinacone hydrate is formed by the action of baryta on the ether obtained by treating tetramethylethene bromide with silver nitrate. W. C. W.

The Order in which the Separation of the Elements of the Hydracids takes place in the Haloïd Derivatives of the Olefines. By H. Eltekoff (*Bull. Soc. Chim.* [2], xxxix, 210—212).—Markownikoff first enunciated the hypothesis that in the separation of hydracids, the hydrogen necessary for their formation is derived from the carbon-group adjoining that which is combined with the halogen, and this has since been shown to be the case by Butlerow, in his researches on isopropylic ether, and by the author, in the formation of ethyl valerate, whilst Saytzeff has since proved that when the carbon-atoms are in different states of hydrogenation, the hydrogen, as a rule, is separated from that carbon-atom which is least hydrogenated.

Reboul has proved that in the case of propylene bromide the elements of the hydracids separate themselves from the carbon-atoms directly linked to the halogens, which the author confirms in the case of isopropylethene bromide. The bromamylene thus obtained consists of a mixture of two isomerides, $(CH_3)_2.CH.CH{=}CHBr$ and $(CH_3)_2.CH.CBr{=}CH_2$, which lose another molecule of hydrobromic acid, and yield the same hydrocarbon isopropyl acetylene,

$$(CH_3)_2.CH.C{\equiv}CH.$$

Similarly the two isomeric bromopropylenes yield the same allylenes. The author has also arrived at the conclusion that in those hydrocarbons derived from acetylene by the replacement of one atom of hydrogen by an alcohol-radicle, the latter remains intact in the hydrocarbon generated. Hydrocarbons derived from ethylene by the displacement of the alcohol-radicles by two hydrogen-atoms combined with the same carbon-atom, can lose only one molecule of an hydracid, whilst those of the formula $R.CH{=}CH.R$ readily form hydrocarbons of the acetylene group. In order to confirm these hypotheses, the author has studied the chemical properties of the valerylene boiling at 51°, to which he assigns the constitution methylethyl-acetylene,

$$C_2H_5.C{\equiv}C.CH_3.$$

On oxidation with chromic mixture it yields propionic and acetic acids.

Its formation from methylethylethene may be thus represented—

$$C_2H_5.CHBr.CHBr.CH_3 = C_2H_5.C{\equiv}C.CH_3 + 2HBr.$$

L. T. O'S.

Action of the Halogens on Guanidine Salts. By J. KAMENSKI (*Deut. Chem. Ges. Ber.*, xi, 619—620).—By the action of a solution of iodine in hydriodic acid on guanidine carbonate, the compound,

$$CN_3H_5.HI + I_2$$

is obtained, crystallising in prisms of the colour of iodine. The corresponding bromine compound, $CN_3H_5.HBr.Br_2$, appears to be produced by the action of bromine (3 mols.) upon guanidine carbonate (1 mol.). It forms large red prisms, which readily lose bromine. If bromine be allowed to react on dry guanidine carbonate in the proportion of equal numbers of molecules, and the product be subsequently decomposed with water, the compound CN_3H_4Br, a monobromoguanidine, is obtained in small yellow needles, which are very difficultly soluble in cold water or in ether, but easily in alcohol. The corresponding chlorine compound, CN_3H_4Cl, has also been obtained.

C. F. C.

Amylidenamine Silver Nitrate. By W. G. MIXTER (*Am. J. Sci.* [3], xv, 205—207).—When a solution of silver nitrate in strong ammonia is mixed with an alcoholic solution of valeral-ammonia, and the mixture is allowed to evaporate spontaneously, crystals are deposited, having the composition $C_{15}H_{33}N_4O_3Ag$. The reactions of this body point to the structural formula,

$$(C_5H_{10})''H_2N.(C_5H_{10})''HN.(C_5H_{10})''NAg.O.NO_2.$$

The new substance is insoluble in water, ammonia, alcohol, and ether, but is readily dissolved by ammoniacal alcohol, from which it may be crystallised. By suspending it in ether, decomposing with sulphuretted hydrogen, filtering, and evaporating, a thick yellowish oil was obtained, having the odour of thiovaleral, and giving numbers, on analysis, pointing to a mixture in the proportion,

$$C_{15}H_{30}N_3 : 2C_5H_{10}S.$$

M. M. P. M.

Oxidation of the Amyl Glycol $(CH_3)_2C(OH)CH(OH)CH_3$. By FLAVITZKY (*Bull. Soc. Chim.* [2], xxix, 214—215).—The oxidation of this amylic glycol takes place at the carbon atoms united with the hydroxyl radicles, with formation of acetone and acetic acid. By the dehydration of the glycol $(CH_3)_2CH.CH(OH).CH_2(OH)$ there is formed, besides valeral, a ketone having the constitution—

$$(CH_3)_2CH.CO.CH_3.$$

Thus it may be inferred that primary secondary glycols yield by dehydration a mixture of aldehydes and ketones.

The amyl glycol $(CH_3)_2.COH.CH(OH).CH_3$ gives rise, by dehydration, to a compound, $(CH_3)_2CH.CO.CH_3$.

L. T. O'S.

Reaction of some Polyatomic Alcohols. By D. KLEIN (*Bull. Soc. Chim.* [2], xxxix, 195—197).—By mixing solutions of mannite and borax of known strength, in different proportions, liquids of different rotatory powers have been obtained, for which the author has constructed two curves: (1) in the case when to a constant volume of a solution of mannite increasing quantities of borax solutions are added, the total volume of the liquid varying in each case; and (2) when increasing quantities of borax solution are added to a constant volume of mannite solution, the total volume being made up in each case to 50 c.c.

In these experiments the author observed that if less than ½ equivalent of borax is added to 1 equivalent of mannite, the solution is acid, but if ½ equivalent of borax is added to 1 equivalent of mannite, the solution remained neutral. At this point, there is an inflection in the curve representing the rotatory power. If alcohol is added to this solution, it yields a compound identical with that formed when equal equivalents of mannite and borax are mixed in solution. If more than ½ equivalent of borax be added for each equivalent of mannite, the solution becomes alkaline.

Similar reactions have been observed when aqueous solutions of borax are added to other polyatomic alcohols, such as glycerin, erythrite, levulose, dextrose, α- and β-galactose, &c. L. T. O'S.

Hydrate of Ether. By C. TANRET (*Compt. rend.*, lxxxvi, 765—767).—By allowing ether to evaporate from a surface of bibulous paper, the author obtains the hydrate, $C_4H_{10}O.2H_2O$, which appears to be of the nature of a cryohydrate, the solid having the temperature $-3{\cdot}5°$, which is the constant minimum obtained by mixing ether and ice. C. F. C.

Formation of Dichloracetic Ether from Chloral. By A. CLAUS (*Deut. Chem. Ges. Ber.*, xi, 498—500).—Wallach has recently (*Ber.*, x, 2120) explained the action of potassium cyanide on chloral, by assuming that hydrocyanic acid in presence of chloral decomposes water, the free hydrogen of which replaces one atom of chlorine in the chloral, while the oxygen converts the aldehyde into acid.

The action of the potassium cyanide is supposed to be due to its being a cyanide, and not in virtue of its alkaline properties. The author differs from Wallach, as he considers that the potassium in the potassium cyanide plays an important part in the reaction, for potassium in potassium cyanide has generally a tendency to exchange cyanogen with the halogen, in an organic chloride, bromide, or iodide.

In the reaction with chloral, the easily oxidisable molecule, in presence of water or alcohol, furnishes disposible hydrogen, which on the one hand displaces the chlorine, and on the other by attraction for the cyanogen of the potassium cyanide, leaves the metal free to combine with the chlorine. W. C. W.

Action of Potassium Cyanide on Dichloracetic Ether. By A. CLAUS and R. WEISS (*Deut. Chem. Ges. Ber.*, xi, 496—498).—When pure potassium cyanide acts on pure dichloracetic ether, hydrocyanic acid is evolved, and the ether is saponified. On long-continued boiling, a complicated decomposition takes place, the mixture blackens, and ammonium carbonate, oxalic and acetic acids are formed.

The dicyanacetic acid described by Amato (*Annalen*, clxii, 389) is not formed in this reaction, and the authors consider that Amato must have used impure materials. W. C. W.

Action of Sulphuryl Chloride on Acetoacetic Ether. By F. Allihn (*Deut. Chem. Ges. Ber.*, xi, 567—570).—Ethylic *acetodichloracetate*, $C_6H_8Cl_2O_3$, described by Conrad (*Annalen*, clxxxvi, 161), is obtained by the action of two molecules of sulphuryl chloride on one of acetoacetic ether, hydrochloric acid and sulphurous anhydride being evolved; but if equal molecules of sulphuryl chloride and of acetoacetic ether are taken, then *ethylic acetomonochloracetate*, $C_6H_9ClO_3$, or $CH_3.CO.CHCl.COOC_2H_5$, is formed. This latter substance is a colourless liquid, which boils at 193—195°, and has a sp. gr. of 1·19 at 14°. Ethylic acetomonochloracetate yields potassium monochloracetate on treatment with alcoholic potash-solution. W. C. W.

Potassium Cyanide and Ethyldibromosuccinate. By A. Claus and F. Calliess (*Deut. Chem. Ges. Ber.*, xi, 496).—Succinic acid is formed by the action of potassium cyanide on ethyldibromosuccinate. The intermediate products of the reaction, viz., dicyanosuccinic acid, and a tetrabasic acid derived from it, could not be isolated. W. C. W.

On Isomeric Caproic Acids. By A. Saytzeff (*Deut. Chem. Ges. Ber.*, xi, 511—513).—*Diethylacetic acid* obtained from the product of the action of potassium cyanide on the iodide of di-ethyl carbinol, is a colourless liquid boiling at 190°. It has a pleasant odour, and is only slightly soluble in water. Its sp. gr. at 18° is 0·9196.

Methylpropylacetic acid, derived from the product of the action of potassium cyanide on amylene hydriodide, closely resembles the preceding acid. It boils at 193°, and its sp. gr. at 18° is 0·9279.

The sp. gr. of *ethylic di-ethylacetate* (b. p. 151°) is 0·8686 at 18°, and that of *ethylic methylpropylacetate* (b. p. 153°) is 0·867 at the same temperature.

The silver salts of these acids are deposited from hot saturated solution, on cooling, as needle-shaped crystals. *Silver di-ethylacetate* is less soluble in cold, but more soluble in hot water than its isomeride.

The barium salts are easily soluble in water and in alcohol. *Barium di-ethylacetate* is crystalline, but *barium methylpropylacetate* forms a thick syrup which dries to a gum-like mass. The solubility of *calcium di-ethylacetate* in water increases with the temperature. *Calcium methylpropylacetate* is less soluble in hot than in cold water. The lead salts are very soft and easily fusible.

The zinc salts dissolve in alcohol; they are more soluble in cold than in hot water. Ferric chloride forms a yellow precipitate with ammonium di-ethylacetate, insoluble in excess, whilst with the methylpropylacetate it produces a flesh-coloured precipitate soluble in excess of the reagent. W. C. W.

Lactic Fermentation. By L. Boutroux (*Compt. rend.*, lxxxvi, 605—607).—The present communication is a continuation of a research published by Pasteur in 1867 (*Ann. Chim. Phys.* [3], lii, 404), and has been carried out under his direction.

A detailed description of the microscopical appearance of the lactic ferment is given. The cells are oval, having a breadth of ·001 to ·0015 mm.; the length is about double this. These organisms develop rapidly when placed in mixtures containing sugar and some nitrogenous matter, such as whey, yeast-water, infusion of malt, or infusion of hay. Inverted sugar or glucose answers best for their growth. A certain amount of acid does not prevent the development of the ferment, although it slightly retards it. The liquor can attain an acidity of 1·5 grams of lactic acid per 100 c.c. If chalk be added in such quantity that the acid becomes neutralised as it is formed, a much larger yield of lactic acid is obtained. If a vessel containing the sugar mixture is sown with the ferment, and the air is then exhausted or displaced by a current of carbonic anhydride free from dust, no fermentation takes place. The ferment is not killed, however, for on re-admitting the air, it again becomes active, and after two or three days forms a film on the surface. When a vessel containing a certain amount of air is sealed up, the growth takes place, but is soon stopped. In a closed flask with pure oxygen, it was found that this gas was entirely absorbed and replaced by carbonic anhydride, which occupied less than one-quarter the volume of the oxygen.

The ferment produces only lactic acid; no alcohol or volatile acid is formed. When the action is completed, the film of the lactic ferment sinks to the bottom of the vessel, but retains its vitality for many months. The formation of spores has not been proved; the cells are preserved without transformation. Besides solutions of sugar, the ferment flourishes in a mixture of yeast-water and alcohol, with or without the addition of acetic acid, or in a mixture of yeast-water and glycol; but then special acids are produced.

The author considers that the lactic ferment and *mycoderma aceti* are identical, but that their functions vary according to the composition of the mixture in which they grow. R. C. W.

Lactic Fermentation of Milk-sugar. By C. Richet (*Compt. rend.*, lxxxvi, 550—552).—Milk which has been kept at a temperature of 40° becomes acid, coagulates, and finally attains an acidity equal to 1·6 grams of lactic acid per 100 of milk, which amount it never exceeds. Moreover, hydrochloric and sulphuric acids, when added in such quantity as to give the milk an acidity equivalent to 1 gram of lactic acid per cent., prevent fermentation. But if instead of a mineral acid, gastric juice is added, the casein is coagulated and finally dissolved, and in less than twenty-four hours the milk contains a larger quantity of acid than it would otherwise have produced in a week. After four or five days an amount of acid corresponding to 4 grams of lactic acid per cent. was found in the liquid. This large increase is probably due to the dissolved casein increasing the fermentation.

When milk is coagulated with rennet and filtered, the whey never gives more than 1·6 grams of lactic acid, even after keeping for six months. The casein, free from lactose, ferments and produces lactic and butyric acids, besides other products of decomposition. If the albuminous substances in milk are coagulated, and it is then evaporated to dryness, and water added in such quantity as to make it up to the original volume, it will not undergo fermentation, even after the addition of pepsin. Whey ferments, although free from casein, because it contains nitrogenous substances in solution, lactoprotein, &c.

A solution of pure lactose will not ferment, nor will a solution of casein in gastric juice; but if these two liquids are mixed, fermentation takes place. A current of oxygen passed through the mixture greatly assists this fermentation.

Phenol added in excess entirely stops fermentation, but if it be added in insufficient quantity, lactic fermentation is only retarded, whereas butyric fermentation is quite checked; a circumstance which may perhaps lead to the separation of these two ferments.

The gastric juice of fish has a similar action to that of mammals, but it requires a temperature of 35° to coagulate the casein.

There is no doubt that, in newly born animals, the rapid acidification of the milk plays a very important part in saving the necessity for a secretion of a large quantity of acid, and that the oxygen contained in the blood greatly assists this rapid fermentation. R. C. W.

Conversion of Acetyl Cyanide into the corresponding Ketone-acid. By J. Claisen and J. Shadwell (*Deut. Chem. Ges. Ber.*, xi, 620—621).—By the addition of concentrated hydrochloric acid (2 mol.) to well cooled acetyl cyanide (1 mol.), the compound $C_3H_5O_2N$ is obtained: isomeric, therefore, and probably identical with the amide of pyroracemic acid. Heated with dilute hydrochloric acid, it is rapidly converted into acetylformic acid, $CH_3.CO.COOH$. This ketone-acid is a liquid boiling at 155—165°, of sp. gr. 1·2415, and yielding a well crystallised silver salt $C_3H_3O_3.Ag$: from the barium salt, by Finckh's method, uvitic acid is easily prepared; thus rendering it probable that the original acid is identical with pyroracemic acid. C. F. C.

Substitution of Oxygen for Sulphur in the Fatty Acids. By A. Dupré (*Compt. rend.*, lxxxvi, 665—668).—If one or two atoms of oxygen in the fatty acids be displaced by sulphur, three series of acids may be obtained: thus $C_nH_{2n+1}.COOH$ being the general formula for the fatty acids, the substituted acids are represented by the formulæ—

$$(1)\ C_nH_{2n+1}.CSOH \qquad (2)\ C_nH_{2n+1}.COSH \qquad (3)\ C_nH_{2n+1}.CSSH.$$

Those of the first series the author calls *sulpho*-acids; their isomerides, the acids of the second series, which have been studied by Kekulé, Ulrich, &c., are the *thio*-acids; whilst the third series are called *thiosulpho*-acids. The author has endeavoured to prepare acids belonging to the first and third series.

With a view to obtain thiosulphopropionic acid, propionitril was heated with an alcoholic solution of sodium hydrosulphide and sulphuretted hydrogen for several days, but it was found that water always took part in the reaction, so that the thiosulphopropionate was not produced. The product separated into two layers, the lower one, on cooling, solidifying to a crystalline mass of sodium sulphopropionate, $C_2H_5.CSONa + H_2O$. It is very soluble in water, less soluble in dilute alcohol, and only sparingly in absolute alcohol. Its aqueous solution possesses the following reactions:—Barium chloride gives a white precipitate; silver nitrate a yellowish-white precipitate, which rapidly decomposes; mercuric chloride a yellowish-white precipitate;

acetate of lead forms a white precipitate not decomposed in the cold, a character by which sulphopropionic acid may be distinguished from its isomeride, lead thiopropionate being decomposed in the cold. When sodium sulphopropionate is treated with $POCl_3$, sulphopropionyl chloride is formed, which proves that the sulphur replaces the oxygen in the group CO.

The author has obtained sodium sulpho-acetate. L. T. O'S.

Glyceric Anhydride. By N. SOKOLOFF (*Deut. Chem. Ges. Ber.*, xi, 679).—An aqueous solution of glyceric acid when evaporated at 100° and left at rest, deposits microscopic crystals of a compound which, by re-crystallisation from water, may be obtained in slender six-sided needles, having the composition $C_3H_4O_3$. This anhydride is insoluble in cold alcohol and in boiling ether; it is soluble in 647 parts of boiling water, by which, moreover, it is but very slowly converted into glyceric acid. C. F. C.

Sulphine-compounds of Thiocarbamide. By A. BERNTHSEN and H. KLINGER (*Deut. Chem. Ges. Ber.*, xi, 492—495).—Methyl iodide slowly combines with thiocarbamide at the ordinary temperature forming *methiodide-thiocarbamide*, $CSN_2H_4.CH_3I$. This substance crystallises in prisms (m. p. 117°), soluble in alcohol and in water. It differs from $CSNH_2.NH.CH_3.HI$, the iodide of methyl-thiocarbamide (m. p. below 100°), in its melting point and its decomposition by silver oxide. Iodide of methyl-thiocarbamide is completely desulphurised by the action of moist silver oxide, methyl-cyanamide being formed. When, however, methiodide-thiocarbamide is treated with silver oxide, a strong base is formed (probably $CSN_2H_4.CH_3OH$), which gives characteristic precipitates with metallic salts. Methiodide-thiocarbamide is decomposed by mercuric oxide forming cyanamide, dicyandiamide, and methyl sulphide. Ethyl iodide readily combines with thiocarbamide at 100° to form ethiodide-thiocarbamide, $CSN_2H_4.C_2H_5I$, first prepared by Claus.

These addition-products are decomposed by heat, hydrocyanic acid being evolved and a residue left which, by treatment with water, may be separated into a difficultly soluble amorphous substance and a compound which is readily soluble and crystallises in needles. The authors consider that these bodies have the constitution—

$$(H_2N)_2C{=}S(C_2H_5)I \quad \text{or} \quad (H_2N)_2C(S.C_2H_5)I.$$

W. C. W.

Hydrocarbon from Betulin. By E. PATERNÒ and P. SPICA (*Gazzetta chimica italiana*, vii, 508—510).—As zeorin, $C_{13}H_{22}O$ (*Gazz.*, vi, 113; this Journal, 1876, ii, 203), and betulin, $C_{12}H_{20}O$, both appear to be homologues of camphor, $C_{10}H_{16}O$, it was of interest to try the effect of dehydrating agents on them. From want of material, the experiment could not be tried with zeorin, but on distilling betulin with phosphoric anhydride, an oil was obtained, which by fractionation yielded a hydrocarbon, boiling at 245—250°, apparently identical with the compound boiling at 243° which Hausmann obtained by the dry distillation of betulin, but to which he assigned the formula, $C_{36}H_{56}O$.

The analyses of the hydrocarbon gave $C = 89{\cdot}23$; $H = 10{\cdot}74$, agreeing with the formula, $C_{11}H_{16}$($C = 89{\cdot}18 : H = 10{\cdot}82$), rather than as might have been expected with $C_{12}H_{18}$, which is that required by the equation, $C_{12}H_{20}O = C_{12}H_{18} + H_2O$. C. E. G.

Action of α-Dinitrochlorobenzene on Urea, Azo-compounds, Aromatic Hydrocarbons, and Sodium Amalgam. By C. WILLGERODT (*Deut. Chem. Ges. Ber.*, xi, 601—605).—*α-Dinitrophenylaniline*, $C_6H_5.NH.C_6H_3(NO_2)_2$, is formed by heating equal weights of α-dinitrochlorobenzene and sulphocarbanilid with alcohol in sealed tubes, at 130—150°. It crystallises in yellow needles, which do not melt at 300°, but decompose with explosion a little above that temperature. *α-Dinitrophenylbromaniline*, $C_6H_4Br.NH.C_6H_3(NO_2)_2$, can be obtained in reddish-yellow crystals (m. p. 152°) by heating a mixture of α-dinitrochlorobenzene and dibromodiphenylcarbamide at 170° in sealed tubes. Bromaniline chloride is formed at the same time. α-Dinitrophenylbromaniline is soluble in hot alcohol, ether, and acetic acid, but is insoluble in hydrochloric acid and water.

α-Dinitrochlorobenzene does not act on azo-compounds, nor does it combine with anthracene. When added to alcoholic solutions of naphthalene and phenanthrene, it unites directly with the hydrocarbons, to form addition-products. The naphthalene-compound forms needle-shaped crystals (m. p. 78°), which are insoluble in ether, alcohol, and glacial acetic acid. The phenanthrene-compound crystallises in orange-coloured needles, which melt at 44°.

Sodium amalgam converts α-dinitrochlorobenzene into a dark brown substance. W. C. W.

Chlorocymene from Thymol and nearly related Bodies. By E. v. GERICHTEN (*Deut. Chem. Ges. Ber.*, xi, 364—369).—When chlorocymene obtained directly from cymene is treated with nitric acid of sp. gr. 1·24, there separates out after five hours' boiling a mass of crystalline needles, consisting of chlorotoluic acid, m. p. 195°. If, however, the chlorocymene obtained from thymol (b. p. 209°) is treated in a similar manner, crystals are deposited on cooling, after 14 days boiling, which have a different composition. These crystals were dissolved in caustic potash, the filtered solution precipitated with hydrochloric acid, and the acid thus obtained purified by means of the barium salt. It crystallises from dilute alcohol in beautiful long needles (m. p. 122°), the analysis of which corresponded with either of the two following formulæ:—$C_6H_3Cl(CH_3).CH_2.CH_2.COOH$, paramethyl-ortho-chloro-hydro-cinnamic acid; or $C_6H_3Cl(C_3H_7).COOH$, chlorinated isomeride of cuminic acid, and not with that of chlorotoluic acid, as formerly supposed (this Journal, p. 49). The barium salt crystallises in pearly plates, with three molecules of water.

The following represents the constitution of the two chlorocymenes, and of the acids which they yield on oxidation:—

Chlorocymene from cymene, ($C_3H_7 : Cl : CH_3 = 1 : 3 : 4$), gives chlorotoluic acid $COOH : Cl : CH_3 = 1 : 3 : 4$).

Chlorocymene from thymol, ($C_3H_7 : Cl : CH_3 = 1 : 2 : 4$), gives an isomeride of chlorocuminic acid, ($C_3H_7 : Cl : COOH = 1 : 2 : 4$), or methyl-chloro-hydro-cinnamic acid ($CH_2.CH_2.COOH : Cl : CH_3 = 1 : 2 : 4$).

Which of the last two formulæ is correct is not yet decided. By treatment with sodium amalgam, either a cuminic acid with normal propyl, or a paramethyl-hydro-cinnamic acid would be produced; whilst by oxidation with permanganate, either the second possible chlorotoluic acid, $C_6H_3Cl(CH_3).COOH$, or $C_6H_3Cl(COOH).C_2H_4.COOH$, or $C_6H_3Cl(COOH)_2$ would result. The author intends preparing the analogous bromine derivative of cymene from thymol, and with it to carry out the above reactions.

Morse and Remsen (*Ber.*, xi, 224; and p. 405 of this volume) have obtained results with para-methyl-ethyl benzene, similar to those described above with para-methyl-propyl-benzene. They treated para-ethyl-toluene with bromine, and oxidised the resulting monobromo-derivative, with formation of bromoparatoluic acid (m. p. 204°). In order to explain this fact, they make use of the supposition first proposed by Remsen, that if a negative atom, as Cl, &c., enter a benzene nucleus in the ortho-position in reference to a side-chain already present, it protects the latter from the influence of oxidising agents; but if a second side-chain be also present in another position, this will be converted by oxidising agents into carboxyl. As, however, this is merely an hypothesis, which has not yet been experimentally proved, the author thinks that Morse and Remsen are not justified in concluding, on the strength of it, that the bromine in brom-para-ethyl-toluene and brom-paratoluic acid is in the ortho-position. Nevertheless the results detailed above with regard to the products of oxidation of the two chlorocymenes, are an important illustration of Ramsen's hypothesis as to the influence of negative atoms in protecing ortho side-chains from oxidation.

The author believes that the chlorotoluic acid (m. p. 185°) prepared by Kekulé and Fleischer from the chlorocymene from carvacrol, is identical with that (m. p. 195°) obtained by himself directly from cymene, and that the difference in melting point is due to an error in Kekulé and Fleischer's determination. T. C.

Method for distinguishing between Orthodiamines and their Isomerides. By A. LADENBURG (*Deut. Chem. Ges. Ber.*, xi, 600).—The hydrochlorides of orthodiamines, when heated with benzaldehyde at 100—120° for a few minutes, evolve hydrochloric acid. Meta- and para-diamines do not exhibit this reaction. W. C. W.

Aldehydines, a New Class of Bases. By A. LADENBURG (*Deut. Chem. Ges. Ber.*, 590—600).—Aldehydine is the name proposed for the class of compounds formed by the union of 1 molecule of an orthodiamine with 2 molecules of aldehyde, the combination being attended by the loss of 1 molecule of water. Meta- and para-diamines do not form stable compounds with aldehydes.

Tolubenzaldehydine, $C_{21}H_{18}N_2$, is prepared by heating benzaldehyde with orthotoluylendiamine at 140°, and may also be obtained by heating the hydrochloride of the base with benzaldehyde, first at 100°, and then at 130°, until hydrochloric acid ceases to be evolved. The crude product is dissolved in hot dilute hydrochloric acid, and the crystals which separate out on cooling are decomposed by ammonia. The free base is soluble in alcohol, acetone, and acids; it is deposited from an alcoholic solution, in transparent, monoclinic prisms, which melt at 195·5°. The base can be sublimed in small quantities, without decomposition. The hydrochloride, $C_{21}H_{18}N_2.HCl.H_2O$, is but slightly soluble in strong hydrochloric acid; it separates out in long, needle-shaped crystals from a solution in the hot dilute acid. The acetate and sulphate could not be obtained in the pure state.

Tolubenzaldehydine Ethiodide.—Two kinds of crystals are produced by the union of ethyl iodide with the aldehydine, viz., thick prisms or tables, and long needles, both of which are soluble in water and in alcohol, and possess the same composition,

$$(C_{21}H_{18}N_2.C_2H_5I.\tfrac{1}{2}H_2O),$$

and melting point (180—181°). An alcoholic solution of iodine converts this compound into $C_{23}H_{23}N_2I_3$, which crystallises in brown plates (m. p. 123°). By the action of silver oxide on tolubenzaldehydine ethiodide an oily liquid is formed, the hydrochloric acid solution of which gives, with platinum chloride, a yellow crystalline precipitate of tolubenzaldehydine ethyl-platinochloride, $(C_{23}H_{23}N_2Cl)_2.PtCl_4$.

Tolubenzaldehydine methiodide forms white, needle-shaped crystals, which melt at 209°, with decomposition. On oxidation with potassium permanganate, tolubenzaldehydine yields an acid, melting at 253·5—254·5°, which is probably dibenzylamidobenzoic acid, $C_{21}H_{14}N_2O_2$.

The preparation of *tolufurfuraldehydine* resembles that of the proceding aldehydine. The pure base crystallises in white, silky prisms (m. p. 115—116°) soluble in alcohol, ether, benzene, toluene, and in acids. The nitrate, $C_{17}H_{14}N_2O_2.HNO_3$, is precipitated on the addition of dilute nitric acid to a solution of the base, the chloride forms a crystalline double salt with platinum chloride, and the sulphate is deposited from an alcoholic solution in prismatic crystals.

Compounds of Orthotolylendiamine with Salicyl Aldehyde.—A substance having the formula, $C_{28}H_{22}N_2O_3$, appears to be formed on heating 1 molecule of orthotolylendiamine with 2 molecules of salicyl aldehyde at 110°, $C_7H_{10}N_2 + 3C_7H_6O_2 = C_{28}H_{22}N_2O_3 + 3H_2O$. It is converted by long continued boiling with hydrochloric acid into an amorphous body; this is soluble in potash-solution, forming a blue fluorescent liquid, from which it is reprecipitated by carbon dioxide.

A substance to which the name *azurine* has been given, is obtained by heating the diamine with twice its weight of the aldehyde at 135°, and extracting the product with hot dilute hydrochloric acid. The acid solution is filtered, and the white amorphous precipitate, thrown down on adding strong hydrochloric acid to the filtrate, is dissolved in alcoholic potash, and shaken up with ether. The ethereal solution is evaporated to dryness, and the residue dissolved in water, precipitated by carbon dioxide, and recrystallised from amyl alcohol. Azurine is characterised by the blue fluorescence of its solutions, and has the composition, $C_{36}H_{32}N_4O_3$; $2C_7H_{10}N_2 + 3C_7H_6O_2 = C_{35}H_{32}N_4O_3 + 3H_2O$. It forms colourless, tabular crystals (m. p. 250·5°), soluble in amyl alcohol and acetone.

Dibenzylidenparaphenylendiamine, $C_{20}H_{16}N_2$, prepared by heating 1 molecule of paraphenylendiamine with 2 molecules of aldehyde at

120°, and extracting the crude product with alcohol, crystallises in scales, which melt at 133—140°. It is soluble in alcohol, petroleum-ether, and acids, but it does not form salts, nor does it form a definite compound with methyl iodide. W. C. W.

Rosaniline. By E. FISCHER and O. FISCHER (*Deut. Chem. Ges. Ber.*, xi, 612—613).—The constitutional formula recently proposed by the authors (*Ber.*, xi, 191) for pararosaniline, viz.,

$$NH_2.C_6H_5{=}C(C_6H_4.NH_2)_2,$$

was based upon the direct conversion into rosaniline of the hydrocarbon diphenylphenylenemethane, $C_{19}H_{14}$, by Hemilian (*Ber.*, vii, 1208). On repeating his researches, however, they find that the product described by him (m. p. 138°) was apparently a mixture of triphenylmethane and the pure hydrocarbon, $C_{19}H_{14}$, which they have obtained crystallised in colourless needles (m. p. 145—146°); the latter is most probably identical with the diphenylenephenylmethane recently prepared by Hemilian from fluorene alcohol. From neither of these have they succeeded in obtaining leucaniline: hence the above formula for para-rosaniline can no longer be maintained. C. F. C.

Ethyl-derivatives of Phenylhydrazine. By W. EHRHARDT and E. FISCHER (*Deut. Chem. Ges. Ber.*, xi, 613—615).—By the action of ethyl bromide upon phenylhydrazine, there is formed in addition to the ammoniacal compound, $C_6H_5.N_2H_2.(C_2H_5)_2Br$, a mixture of volatile bases, from which the authors have isolated the following compounds:—1. A tertiary hydrazine base, which has not been further investigated. 2. *Diethyl-diphenyltetrazone*, $(C_2H_5)_2{=}N{-}N{=}(C_6H_5)_2$. 3. *Azophenylethyl*, $C_6H_5.N{=}N.C_2H_5$. This compound, the simplest representative of the mixed azo-bodies, is a yellow oil, which may be distilled unchanged. It is dissolved by hydrochloric acid, and the solution is decomposed on boiling; by the action of reducing agents on its alcoholic solution it is converted into the hydrazine base $C_6H_5.NH.NH.C_2H_5$. This distils unchanged, and forms easily soluble salts. C. F. C.

Action of Nitrous Acid on Benzene-sulphinic Acid. By W. KOENIGS (*Deut. Chem. Ges. Ber.*, 615—619).—By the action of nitrous acid (1 mol.) upon benzenesulphinic acid (2 mols.), the author has obtained the compound $(C_6H_5.SO_2)_2.HNO$, crystallising from its solution in alcohol in large, colourless prisms. It is almost insoluble in water, but soluble in alcohol and in ether, and somewhat less so in benzene and in chloroform. This body appears to be a mixed anhydride of nitrous acid and the sulphinic acid, into which it is resolved by the action of alkaline solutions. Boiled with water and aniline hydrochloride, it yields phenol. If this body be added in slight excess to a solution of potassium or barium hydroxide, and, after filtration, decomposed with aniline hydrochloride, a mixture of diazoamidobenzene and diazobenzene-benzene sulphinate is precipitated. The compound $(C_6H_5SO_2)_2HNO$, when heated with sulphuric acid, appears to yield hydroxylamine. This fact indicates the possibility of its synthesis from benzene sulphochloride and hydroxylamine. By further treatment of its alcoholic solution with nitrous acid, it is converted into the compound $C_{18}H_{15}NS_3O_7 = (C_6H_5SO_2)_3NO$, a crystalline body, melting at 98°, and insoluble in alkalis. C. F. C.

Iodated Derivatives of Phenols. By H. KÄMMERER and E. BENZINGER (*Deut. Chem. Ges. Ber.*, xi, 557—561).—The addition of a solution of iodine in iodide of potassium to a hot dilute alkaline solution of phenol produces a red precipitate; in a similar solution of thymol a pale-violet precipitate; and in a solution of commercial creosote it produces first a greenish-brown fluorescent coloration, and finally a bulky brown precipitate.

The phenol derivative is prepared by adding excess of iodine (70—75 grams dissolved in 600 c.c. of water, containing 45 grams of potassium iodide) to a boiling solution of 300 grams of soda-crystals and 10 grams of phenol in 1 litre of water. After removing the excess of iodine, by adding 30 grams of soda-crystals to the boiling mixture, the reddish-brown precipitate is collected on a filter. Alcohol extracts from the filtrate, which should be colourless, a white crystalline compound (m. p. about 150°), probably di-iodo-diphenylhydroquinone $(HO)IH_3C_6 + C_6H_3I(OH)$. This body is at once converted into the insoluble red compound, by boiling with iodine and sodium carbonate.

The red substance is identical in its properties with a compound obtained by the decomposition of tri-iodophenol and tri-iodosalicylic acid, to which the formula $C_2H_2I_2O$ was assigned by Lautemann (*Annalen*, cxx, 137) and Kekulé (*ibid.*, cxxxi, 221). The authors, however, regard it as *tetra-iododiphenylenequinone* $C_{12}H_4I_4O_2$, since it is converted into the hydroquinone $C_{12}H_6I_4O_2$ by the action of sulphurous acid; its formation from tri-iodophenol and from phenol is explained by the following equations:—

$$2C_6H_2I_3OH + 2KHO = 2KI + 2H_2O + C_{12}H_4I_4O_2.$$
$$2C_6H_5OH + 12I + 4Na_2CO_3 = C_{12}H_4I_4O_2 + 8NaI + 4CO_2 + 4H_2O.$$

W. C. W.

Etherification of Phenols. By MENSCHUTKIN (*Deut. Chem. Ges. Ber.*, xi, 679).—The etherification of phenols resembles that of tertiary alcohols. The following are the initial velocities and limits of etherification as determined for the following phenols:—

	Initial velocity.	Limits.
Phenol	1·45	8·61
Paracresol	1·40	9·54
Thymol	0·55	9·18
Naphthol	—	6·16

C. F. C.

Thymol Derivatives. By L. BARTH (*Deut. Chem. Ges. Ber.*, xi, 567).—Four acids are formed by fusing thymol with potassium hydroxide, viz.:—(1) oxybenzoic acid; (2) Burkhardt's oxyterepthalic acid; (3) an acid forming needle-shaped crystals (m. p. 143°), which has the composition $C_{10}H_{12}O_3$, and which it is proposed to call *thymoloxy-*

cinnamic acid; (4) a bibasic acid, $C_{10}H_{10}O_3$, which is difficult to obtain in the pure state. It is easily soluble in water, and the aqueous solution precipitates lead salts, and gives an intense red coloration with ferric chloride. The author proposes to call this substance *thymolic* acid.
W. C. W.

Mononitropyrocatechin. By R. BENEDIKT (*Deut. Chem. Ges. Ber.*, xi, 362—363).—This compound is produced by dissolving 4 grams of pyrocatechin and 20 grams of potassium nitrite in 150 c.c. of water, and adding dilute sulphuric acid until effervescence ceases. The dark-brown red liquid obtained is exhausted with an equal volume of ether, and the residue left on distilling off the latter recrystallised several times from hot benzene.

Mononitropyrocatechin, $C_6H_3.NO_2(OH)_2$, crystallises in small yellow silky needles, which dissolve easily in water, alcohol, and ether, but are very difficultly soluble in benzene. It melts at 157° and dissolves in caustic potash with a beautiful purple colour.

Barium salt, $C_6H_3(NO_2)O_2Ba + 3H_2O$, crystallises in dark-red plates, with metallic lustre. It is very difficultly soluble even in boiling water. On drying at 130°, it loses its water of crystallisation and becomes dark green.

Mono-amido-pyrocatechin, $C_6H_3(NH_2).(OH)_2$, is produced by the action of reducing agents on the nitro-compound. The hydrochloride crystallises in long dark needles. On attempting to obtain the free base from this salt by treating it with caustic or carbonated alkalis, it oxidises immediately on contact with the air, and dissolves with a dark violet colour.

A second nitropyrocatechin has been obtained in small quantity, but has not yet been completely investigated. It distils with steam, is very difficultly soluble in water, and forms yellow drops which, after a time, solidify to a crystalline mass.
T. C.

A Quinone Derivative occurring in Agaricus Atrotomentosus. By W. THÖRNER (*Deut. Chem. Ges. Ber.*, xi, 533—535).—On treating *Agaricus atrotomentosus* with ether, a wine-red solution is obtained, which on evaporation leaves a dark-brown crystalline mass, soluble in solutions of caustic alkalis. By dissolving the precipitate, which is produced on adding hydrochloric acid to this alkaline solution, in boiling glacial acetic acid, *α-dioxyquinone*, $C_{11}H_6O_2(OH)_2$, is obtained in the pure state, in the form of dark-brown shining plates (m. p. above 360°). It is insoluble in water, benzene, petroleum-ether, chloroform, and carbon bisulphide, and dissolves with difficulty in boiling alcohol and in glacial acetic acid, forming red solutions. The substance dissolves in alkalis, forming a yellowish-green liquid, which becomes colourless when boiled with zinc dust. Oxidation takes place on exposure to the air, and the solution assumes its original colour. The addition of ammonia to the red alcoholic solution first changes the colour to violet, which passes into dark blue, green, and finally yellow. The acetate, $C_{11}H_6O_2(C_2H_3O_2)_2$, forms reddish-yellow crystals, which melt at 238—240°.

Agaricus atrotomentosus, *Ag. bulbosus*, and *Ag. integer* contain bodies which form crystalline double salts with platinum chloride. The last-mentioned fungus also contains considerable quantities of mannite.

W. C. W.

Aurin. By E. and O. FISCHER (*Deut. Chem. Ges. Ber.*, xi, 473).—Triphenylmethane is formed by the action of alcohol on the diazo-compound of leucaniline prepared from pure aurin. This confirms the authors' view of the constitution of aurin, viz., that it has the formula $C_{19}H_{14}O_3$, and is a derivative of triphenylmethane.

W. C. W.

Action of Boron Fluoride on Anethol.—Properties of Hydroboric Fluoride. By F. LANDOLPH (*Compt. rend.*, lxxxvi, 601—604).—Anethol is instantaneously polymerised by fluoride of boron at the ordinary temperature, but at the boiling heat the action is different. In this way the author obtained anisol, C_7H_8O, and another substance, $C_{11}H_{16}O$, boiling at 225—228°, having a powerful odour, resembling that of camphor. *Hydroboric fluoride*, $BFl_3.3HFl$, is formed at the same time, and was easily isolated, distilling at about 130°, although no constant boiling point could be observed: its vapour-density was found to be 4·72, that calculated for 2 volumes being 4·42. The splitting up of anethol by the action of fluoride of boron is represented by the equation:—

$$C_{20}H_{24}O_2 = C_7H_8O + C_{11}H_{16}O + C_2.$$

The author's former communications on anethol are referred to in *Compt. rend.*, 1875, 12 Juillet; 1876, 17 Janvier, and 10 Avril; and this Journal, 1876, i, 246, 705, ii, 79.

R. R.

Melilotol. By T. L. PHIPSON (*Compt. rend.*, lxxxvi, 830—831).—Melilotol is an oily product found together with coumarin in the *Melilotus officinalis*, and may be extracted by distilling the plant (when in flower) with water, agitating the aqueous distillate with ether, and allowing the ethereal solution to evaporate spontaneously. It has an agreeable odour, is but very slightly soluble in water, very soluble in alcohol and ether, and when boiled with a concentrated solution of potassium hydroxide, yields *melilotic acid*, $C_9H_{10}O_3$, which is also found in the plant. The formula of melilotol the author states to be $C_9H_8O_2$. He believes it to be analogous to salicylic aldehyde, and that to it the agreeable odour of the *M. officinalis* is due. Coumarin, $C_9H_6O_2$, when treated with sodium amalgam in presence of water, gives melilotic acid, the reaction being:—

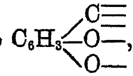
$$C_9H_6O_2 + H_2 = C_9H_8O_2 : C_9H_8O_2 + H_2O = C_9H_{10}O_3;$$

the melilotol, as it is produced uniting with the elements of water, to form melilotic acid.

C. E. G.

Salicylic Acid. By J. WILLIAMS (*Pharm. J. Trans.* [3], viii, 785—786).—The author, on comparing the physical and chemical properties of the natural and artificial salicylic acid, found that they differed, owing to the presence in the artificial acid of an impurity which he calls cresyl-salicylic acid. When purified, the natural and artificial acids exhibit identical properties. The purification is effected by dissolving the acid in boiling water, and neutralising it with calcium carbonate. On cooling, calcium salicylate crystallises out, and is purified by repeated crystallisation from hot water. When this is decomposed with hydrochloric acid, and the precipitated salicylic acid is recrystallised from hot water, and finally from dilute alcohol, it is obtained in large white crystals similar to those of the natural acid.

Cresyl-salicylic acid is obtained from the uncrystallisable portion of the mother-liquor from the calcium salicylate, by decomposition with hydrochloric acid, but the author has not completed the investigation of this body. L. T. O'S.

Protocatechuic Series of Compounds. By F. TIEMANN (*Deut. Chem. Ges. Ber.*, xi, 659—675).—The relations existing between the compounds containing the common group  $C_6H_3\begin{cases}C\equiv\\O-\\O-\end{cases}$, and derivable therefore from protocatechuic acid, may be classified in four parallel series, viz. (1.) The *protocatechuic* acid series proper, the members of which contain a single carbon atom, $-C\equiv$, in the side chain. (2.) The *α-homoprotocatechuic* series, of which the characteristic group is the side chain containing $-CH_2-C\equiv$. (3.) The *hydrocaffeic* series of bodies containing in the side chain the group $-CH_2-CH_2-C\equiv$. (4.) The *caffeic*, with the side chain group $-CH{=}CH-C\equiv$. Tables of the acids, alcohols, aldehydes, &c., of these series are given, with the melting points, as far as they are known, from an inspection of which it is evident that the higher homologues in the several series melt at a lower temperature than the lower; also that the melting points of members of the caffeic is uniformly higher than those of corresponding members of the hydrocaffeic series; and that of those acids which contain a single methoxyl group, those in which the latter group occupies the para-position in relation to the side chain, melt at a higher temperature than those in which the meta relation obtains. To each of the acids of the above series corresponds an aldehyde, alcohol, and a body resulting from the replacement of carboxyl by methyl.

Constitution of Eugenol.—The question of the constitution of eugenol resolves itself into that of its side chain, the group C_3H_5. From the formation of acetic acid in the oxidation of the oil, Erlenmeyer inferred the presence of the group CH_3-C, and hence considered it as having the constitution $-CH{=}CH-CH_3$. He, however, has since shown (*Ber.*, ix, 273) that acetic acid is a product of the oxidation of the oxybenzoic acids, and that the above conclusion is not warranted. On this ground, together with the fact that the formation of acet(α)-homovanillic acid from aceteugenol is irreconcilable with this view, it is rejected by him, and the formula $-CH_2-CH{=}CH_2$, proposed for the side group. To this the author takes objection, maintaining the original formula on the following grounds:—Eugenol, coniferyl alcohol, and ferulic acid all yield vanillin as a product of limited oxidation, apparently in the same way that cinnamic acid and anethol yield benzaldehyde and anisaldehyde respectively, a result which indicates an analogous constitution of the side chains. These reactions, as well as the formation of veratroyl-carbonic acid from methyl-eugenol, are explained with difficulty on Erlenmeyer's hypothesis.

The following series of reactions (in which $R = $ the C_3H_5 group), explaining the derivation of vanillin, and similarly of α-homovanillin, are fully discussed by the author:—

$$\begin{array}{ll}(1) & R.CH{=}CH.CH_3 + H_2O = R.CH(OH).CH_2.CH_3 \\ (2) & R.CH(OH).CH_2.CH_3 + O = R.CO.CH_2.CH_3 + H_2O \\ (3) & R.CO.CH_2.CH_3 + H_2O = R.COH + CH_3.CH_2OH.\end{array}$$

The author hopes to verify this view of the constitution of eugenol by effecting the following reaction:—

$$\{C_6H_3(\overset{m}{O}CH_3)(\overset{p}{O}H)CH{=}CH{-}CH_2.COOH\} - CO_2 = \\ C_6H_5(OCH_3)(OH)CH{=}CH{-}CH_3,$$

analogous to that of the conversion of phenylcrotonic acid into anethol (Perkin, *Journ. Chem. Soc.*, 1877, i, 412), but has not as yet obtained the acids in sufficient quantity.

Constitution of Coniferyl Alcohol.—The author in reply to certain objections urged by Erlenmeyer (*Ber.*, x, 630), discusses the formula proposed by himself for coniferyl alcohol,

$$C_6H_3(OCH_3)(OH)CH{=}CH{-}CH_2OH,$$

in relation to its decomposition:—

(1.) By chromic acid, with formation of acetic acid and ethaldehyde. This might be supposed to be due to the union of the $CH{=}CH$ group with water to form ethaldehyde, but the author does not consider this to be the case. He has, however, shown experimentally that acetic acid is not formed as a product of the reaction of the benzene nucleus with the elements of water, and concludes, therefore, that the reaction in question must be confined to the side chain.

Coniferyl alcohol, when boiled with dilute sulphuric acid, yields a small quantity of vanillin, from which reaction, bearing in mind the ease with which mixed aromatic and fatty ketones are decomposed, with formation of aromatic aldehydes, the presence of the $—CO.CH_2.CH_3$ group might be inferred: on the other hand, the minuteness of the quantity of vanillin produced, the analogy of coniferyl to cinnamyl alcohol, and the tendency of the former to polymerisation, favour the original hypothesis. The formation of vanillin is explained by the hydration of coniferyl alcohol to form the compound

$$C_6H_3(OCH_3)(OH).CH(OH).CH_2.CH_2(OH),$$

which is resolved into vanillin and ethyl alcohol in the same way that lactic acid splits up into ethaldehyde and formic acid.

(2.) By fuming hydriodic acid, with formation of methyl and ethyl iodides. The production of the latter compound is referred to the decomposition of the side chain. That this is its actual origin is rendered probable by the observation of Hlasiwetz (*Annalen*, cxlii, 227) of the conversion of caffeic acid, $C_6H_3(OH)_2.CH{=}CH.COOH$, into homopyrocatechin, $C_6H_3(OH)_2.CH_3$, by the action of hydriodic acid.

Nevertheless, Erlenmeyer failed to obtain ethyl iodide from cinnamyl alcohol by a similar reaction: but the author on repeating the experiment, has obtained results which are reconcilable with the original formula for coniferyl alcohol.

Action of Hydriodic Acid upon Cinnamyl Alcohol.—By the action of fuming hydriodic acid (25 parts) upon cinnamyl alcohol (10 parts) at 180—200°, in sealed tubes, the author has obtained a mixture of toluene and phenylpropylene. The first stage of the reaction probably consists in the formation of the latter body, which is decomposed by the prolonged action of the hydriodic acid according to the equation:—

$$C_6H_5.CH{=}CH.CH_3 + 3HI = C_6H_5.CH_3 + CH_3.CH_2I + I_2.$$

From this it is a direct inference, that coniferyl alcohol would yield, when similarly treated with hydriodic acid, a dioxyphenylpropylene, $C_6H_3(OH)_2.CH{=}CH.CH_3$; and a dioxytoluene (homopyrocatechin). The author appears to have identified the latter body amongst the products of this reaction, but the dioxyphenylpropylene is so very unstable that it could not be isolated, the chief product being an almost insoluble resinous substance containing considerable quantities of iodine. C. F. C.

Diaceto(α)homoprotocatechuic Acid. By Nagajosi Nagai (*Deut. Chem. Ges. Ber.*, xi, 658).—This acid is easily prepared by the action of acetic anhydride, at its boiling temperature, upon α-homoprotocatechuic acid. It occurs in the form of minute crystals which melt at 89—90°, and are soluble in water, alcohol, and ether. It does not give any reaction with ferric chloride. C. F. C.

Synthesis of Caffeic Acid, and Derivatives of Caffeic and Hydrocaffeic Acids. By F. Tiemann and Nagajosi Nagai (*Deut. Chem. Ges. Ber.*, xi, 646—657).—The direct and collateral results of this research are given under the successive compounds investigated:—

Acetovanillin, $C_6H_3.(COH).(O.\overset{m}{C}H_3)(O.\overset{p}{C}_2H_3O)$, is best prepared by allowing the sodium-compound of vanillin to remain in contact with an ethereal solution of acetic anhydride for some hours. It forms large flat needles which melt at 77°; it is easily soluble in alcohol and ether, but only sparingly in water.

Acetoferulic acid, $C_6H_3(CH{=}CH.COOH)(O.\overset{m}{C}H_3)(O.\overset{p}{C}_2H_3O)$, is formed by heating either vanillin or the preceding compound with anhydrous sodium acetate and acetic anhydride. It crystallises in slender needles melting at 196—197°: it is readily soluble in alcohol and in ether, but with difficulty in water.

Ferulic acid, $C_6H_3.(CH{=}CH.COOH)(O.\overset{m}{C}H_3)(\overset{p}{O}H)$, results from the decomposition of the preceding compound by sodium hydrate. This synthetic acid crystallises from boiling water in brittle prisms of high refractive power which melt at 168—169°. The authors have isolated ferulic acid from assafœtida according to the method of Hlasiwetz and Barth, and find that it also melts at 168—169°, and not at 153° as stated by them. In order, finally, to establish the identity of these products, (1) the latter was heated with acetic anhydride, and found to yield a body identical in all respects with the acetoferulic acid described above, and (2) the acetoferulic acid thus prepared from the "natural" acid was oxidised by potassium permanganate in acetic acid solution, and found to yield acetovanillin and acetovanillic acid.

In ferulic acid the hydrogen both of the carboxyl group and of the phenolic hydroxyl is capable of being replaced by metals, so that it yields two classes of salts, of which the primary ammonium and secondary potassium salts have been obtained by Hlasiwetz. Ferulic acid is a hydroxyl-methoxyl-cinnamic acid, and can readily take up two hydrogen atoms, forming hydroferulic acid.

Hydroferulic acid, $C_6H_3(CH_2.CH_2.COOH)(\overset{m}{O}CH_3)(\overset{p}{O}H)$, is easily obtained by the action of reducing agents upon ferulic acid. It crystallises from its aqueous solution in microscopic plates (m. p. 89—90°) which are very easily soluble in alcohol, ether, and hot water. Like the preceding it forms two classes of salts.

Dimethylcaffeic acid, $C_6H_3(CH{=}CH.COOH)(\overset{m}{O}.C\overset{p}{H}_3)_2$, or *methylferulic acid*, was prepared by the authors by two parallel methods, namely, by replacing the two hydroxyl groups of caffeic or dioxycinnamic acid, and the single hydroxyl group of ferulic acid by methoxyl, by heating them with potash and methyl iodide, in methyl alcohol solution; the acids thus obtained are identical in every respect, thus establishing beyond doubt the constitutional relations of the three acids. Dimethylcaffeic acid crystallises in needles which melt at 180—181°. It is a monobasic acid. The salts which it forms with the metals of the alkalis and alkaline earths are readily soluble.

Hydrodimethylcaffeic acid, $C_6H_3(CH_2.CH_2.COOH)(\overset{m}{O}C\overset{p}{H}_3)_2$, was obtained by reduction from dimethylcaffeic acid prepared both from ferulic acid and from caffeic acid: the products were identical. This acid crystallises from its aqueous solution in slender needles which melt at 96—97° to an oil which solidifies at 60°.

Isoferulic acid, $C_6H_3(CH{=}CH.COOH)(\overset{m}{O}H)(O\overset{p}{C}H_3)$, is formed by heating caffeic acid with methyl iodide and potassium hydrate in insufficient quantity for the complete replacement of its hydroxyl. The methyl ethers of isoferulic and dimethylcaffeic acids are thus obtained: they are easily separated, and the isoferulic acid may be isolated, after saponification, in the form of crystals which melt at 211—212°. It forms two classes of salts.

Hydroisoferulic acid, $C_6H_3(CH_2.CH_2.COOH)(\overset{m}{O}H)(O\overset{p}{C}H_3)$, is readily formed from the preceding acid by reduction. The pure acid forms slender colourless needles which melt at 146° to an oil which solidifies at 130°.

Synthesis of Caffeic Acid.—By means of the action of sodium acetate and acetic anhydride on protocatechuic aldehyde, the authors have converted the latter into a diacetocaffeic acid, identical in all respects with that obtained by the action of acetic anhydride on caffeic acid: thus finally establishing the constitution of the latter acid.

The *diacetocaffeic acid*, $C_6H_3(CH.CH.COOH)(\overset{m}{O}C_2H_3\overset{p}{O})_2$, crystallises in slender needles which melt at 190—191°. It is readily converted into caffeic acid by heating it with a solution of potassium hydrate. C. F. C.

The Tannin of Ilex Paraguayensis. By P. N. ARATA (*Gazzetta chimica italiana*, vii, 520—530).—The tannin from Maté or Paraguay tea has hitherto been considered as identical with the caffeotannic acid from coffee, but on making a careful comparison of the two the author finds there is, in many respects, a difference between them.

I. The tannin in both cases was extracted by means of dilute alcohol, and the solution, after the addition of a little subacetate of lead and filtration, was precipitated by lead acetate. This precipitate was decomposed by sulphuretted hydrogen, the solution evaporated at 100°, and again dissolved and precipitated by lead acetate, &c., the operation being repeated several times.

II. The chief differences in the behaviour of the two tannins with reagents were as follows:—

	Caffeotannic acid.	Ilex tannin.
Acetate of lead ..	Bright yellow pp.	Greenish-yellow pp.
Baryta water	Yellow pp.	Green pp.
Gelatin solution..	Slight pp.	Abundant pp.

III. By dry distillation, caffeotannic acid gives pyrocatechin, and ilex tannin also gives a distillate having the reactions of pyrocatechin, but the crystals obtained from it are very soluble in ether, and only slightly soluble in water, whilst pyrocatechin is very soluble.

IV and V. The solubility of the two tannins in alcohol differs, the ilex tannin being much less soluble. The analytical results obtained by the author for the ilex tannin also differ from those obtained by Rochleder and by Payen for caffeotannic acid; as the carbon in the three analyses given, however, is 40·49, 50·24, and 48·30 respectively, the evidence of a difference in composition can scarcely be considered as conclusive, although they are all considerably below that obtained from caffeotannic acid ($C = 56{\cdot}35$).

VI. Heated with a strong solution of potassium hydroxide, as in the preparation of caffeic acid from caffeotannic acid, ilex tannin yields a similar compound, but differing from caffeic acid in its reactions. The two tannins, after fusion with potassium hydrate, neutralisation with acid, and extraction with ether in the usual way, both gave crystalline products; these, however, differed somewhat, the protocatechuic acid from caffeotannic acid giving a white precipitate with silver nitrate, and a red colour with mercurous nitrate, whilst the product from the ilex tannin gave no precipitate with silver nitrate, and a yellowish colour with the mercurous salt.

VII. The ilex tannin appears to be a glucoside as, after being boiled with an acid or an alkali, the solution reduces Fehling's test: this sugar is uncrystallisable. The author believes the tannin, when free from sugar, to be like gallotannic acid (digallic acid), a polyacid ether, or rather a mixture of polyacid ethers. C. E. G.

Oxytoluic and Oxyphthalic Acids. By O. JACOBSEN (*Deut. Chem. Ges. Ber.*, xi, 374—381).—Each of the four xylenols recently described by the author yields, on fusion with potassic hydrate, an oxytoluic and an oxyphthalic acid. The present communication refers to those obtained from the liquid (1 : 3 : 4) metaxylenol. The fused mass obtained in the above manner from (1 : 3 : 4) xylenol was dissolved in water, saturated with hydrochloric acid, and exhausted with ether: the acids were removed from the ethereal solution by caustic soda, and precipitated from the alkaline solution by hydrochloric acid in crystalline flocks. They were separated by distillation in steam, when the oxytoluic acid passed over in the distillate, leaving the oxyphthalic acid behind. The former was purified by recrystallisation.

Oxytoluic acid, $C_6H_3(CH_3)(COOH)(OH)$.—It is easily soluble in alcohol, ether, and hot water, but only slightly in the cold. It crystallises from petroleum ether in long needles (m. p. 149°). The aqueous solution of the acid or of its salts gives a deep violet-blue coloration with ferric chloride.

Barium salt $(C_8H_7O_3)_2Ba.2H_2O$, is easily soluble in water, and crystallises in large arborescent groups of plates with silvery lustre.

Normal copper salt decomposes easily.

The formation of the acid from (1 : 3 : 4) metaxylenol shows that only the two following formulæ are possible, viz.:—$CH_3 : COOH : OH =$ (1 : 3 : 4), or (1 : 3 : 5).

The acid when heated with strong hydrochloric acid at 180—185°, in sealed tubes was easily split up into carbonic anhydride and a cresol, which, after purification, distilled at 200°, and crystallised in large rhombic plates, melting at 35°. This cresol, on fusing with caustic potash, was oxidised to para-oxybenzoic acid (m. p. 210°). This fact, together with its other properties, proves that it was paracresol, and therefore that the oxytoluic acid (m. p. 149°) is represented by the first of the above formulæ. It is consequently identical with that obtained by Engelhardt and Latschinoff (*Zeitschr. f. Chem.* (1869), 622) from paracresol, and by fusing crude potassium xylolsulphate with potash. Fittica has also arrived at a similar constitution for this body (*Ber.*, vii, 928). Not para-, but ortho-cresol appears to be obtained, however, when the calcium salt of this oxytoluic acid is distilled with excess of lime. The product is an oil which solidifies to a crystalline mass melting at about 15°, and when oxidised by fusion with potash, yields salicylic acid, and not a trace of paraoxybenzoic acid.

The *Oxyisophthalic acid*, $C_6H_3(OH)(COOH)_2$, obtained together with the oxytoluic acid as above described, crystallises from its hot aqueous solution in colourless needles, and from hot dilute alcohol in small prisms. 160 parts water at 100° dissolve one part of the acid. It is easily soluble in alcohol, less so in ether, and not at all in chloroform. Very dilute solutions of the acid or its salts give a cherry-red coloration with ferric chloride, which is not destroyed by boiling or hydrochloric acid. It melts at 284° (corrected), is decomposed at 295°, and sublimes slightly at 220°.

The *sodium salt* crystallises very easily from water in long, flat needles, containing water of crystallisation, which it loses slowly and partially in dry air at the ordinary temperature, and completely at a gentle heat.

The *barium salt* crystallises in small needles.

The cadmium, cobalt, copper, and neutral and acid silver salts were also prepared.

The *dimethyl ether* crystallises from dilute methyl alcohol in large flat needles, m. p. 96°.

The *diethyl ether* crystallises from the warm aqueous solution in needles, m. p. 52°.

The *amide*, $C_6H_3(OH)(CO.NH_2)_2$ (m. p. 250°), separates from hot alcohol in minute rhombic plates, which are difficultly soluble in hot alcohol, and almost insoluble in cold alcohol or in water.

The constitution of oxyisophthalic acid follows from that of liquid metaxylenol, *i.e.*, its side chains are in the positions 1 : 3 : 4. By treatment with strong hydrochloric acid at 180°, it forms a colouring-matter similar to aurin, which crystallises from alcohol in needles having a green metallic lustre, and giving with alkalis a red coloration.

This oxyisophthalic is doubtless identical with the orthophenoldicarbonic acid obtained by Ost (*J. pr. Chem.* [2], xiv, 103) from salicylic and carbonic acids, also with the α-oxyisophthalic acid produced by Tiemann and Reimer (*Ber.*, x, 1571) on oxidising paraaldheydo-salicylic and ortho-aldehydo-paraoxybenzoic acids, which proves therefore that the constitution of the two latter bodies is 1 : 3 : 4.

Paraxylenol, on fusion with caustic potash, yields an oxytoluic acid (m. p. 174°) and an oxyterephthalic acid, already described by Burkhardt; whilst (1 : 2 : 4) orthoxylenol, under similar circumstances, gives an oxytoluic acid (m. p. 198°) and an oxyphthalic acid, which is not identical with that obtained by Baeyer. The author is still investigating the nature of these products. T. C.

Oxytoluic and Oxyphthalic Acids. By O. JACOBSEN (*Deut. Chem. Ges. Ber.*, xi, 570—574).—By long-continued fusion with caustic potash, paraxylenol yields Burkhardt's oxyterephthalic acid (*Ber.*, x, 144) and an oxytoluic acid (m. p. 177°) identical with that obtained by Engelhardt and Latchinoff (*Zeitschr. f. Chem.*, 1869, 623), and by Oppenheim and Pfaff (*Ber.*, viii, 889) from metacresol. The same oxytoluic acid is formed by the oxidation of metahomosalicyligenic acid. This acid must be $CH_3 : OH : COOH = 1 : 3 : 4$; since it is formed both by the introduction of the carboxyl group into metacresol, and by the oxidation of one of the methyl groups in paraxylenol. By heating with hydrochloric acid at 170°, oxytoluic acid is decomposed into metacresol and carbon dioxide.

Thymol is decomposed by fusion with caustic potash into acetic, oxytoluic, and oxyterephthalic acids. Carvacrol treated in this way gives no acetic acid, but oxyterephthalic acid and an iso-oxycinnamic acid. This is a crystalline body (m. p. 93°), which volatilises in a current of steam, and gives a reddish-violet coloration with ferric chloride.

The author thinks it probable that in this acid the groups OH, COOH, and CH_3 have the position 1 : 3 : 4, whilst in *metahomoparaoxybenzoic acid* they are 1 : 4 : 3.

W. C. W.

A New Mode of Formation of α-Oxyisophthalic Acid (α-Phenol-dicarbonic Acid. By M. W. ILES and I. REMSEN (*Deut. Chem. Ges. Ber.*, xi, 579—582).—Sulphamin-isophthalic acid, obtained by oxidising para-sulphamine-toluic acid with potassium permanganate, yields when fused with potash, α-phenol dicarbonic acid, which has been described by Ost (*J. pr. Chem.*, xiv, 93, and xv, 301) and by Tiemann and Reimer (*Ber.*, x, 1571). Since α-phenol dicarbonic acid has the constitution $C_6H_3(COOH)(COOH).OH$ (1 : 3 : 4), it follows that sulphamin-isophthalic acid is

$$C_6H_3(COOH)(COOH).SO_2NH_2$$

(1 : 3 : 4), and parasulphamintoluic acid $C_6H_3(CH_3)(COOH).SO_2NH_2$ (1 : 3 : 6), and consequently the position of the side chains, CH_3, CH_3, and NH_2SO_2, in the xylenesulphamide, which melts at 95—96°, must be (1 : 3 : 6), as previously stated by the authors (*Ber.*, x, 1042), and not (1 : 3 : 2) as contested by Jacobsen (*ibid.*, xi, 17).

W. C. W.

Behaviour of Benzoic Acid in the Organism of Birds. By M. JAFFE (*Deut. Chem. Ges. Ber.*, x, 1925—1930).—The author confirms Shepard's result, that no hippuric acid is produced by the decomposition of benzoic acid administered to birds. The main product of the decomposition is a new body, for which the name of *ornithuric acid* is suggested. The new acid is extracted from the excrement of birds, to which benzoic acid has been administered, by boiling with alcohol, evaporating, extracting fat, &c., with ether, acidulating with sulphuric acid, and again shaking up with ether: the dark-coloured mass, which separates on cooling the ethereal liquid, is purified by a tedious process. Ornithuric acid crystallises in very small, colourless needles, insoluble in ether, soluble with difficulty in water, somewhat soluble in acetic ether, soluble in hot alcohol; the crystals melt at about 182°. The formula assigned to the acid is $C_{19}H_{20}N_2O_4$. By the action of boiling hydrochloric acid, ornithuric acid yields benzoic acid.

In the purification of ornithuric acid, a new base was obtained. This substance could not be perfectly purified, but from a study of its compounds with acids, it is shown to have the formula $C_5H_{12}N_2O_2$. The base is a crystalline substance, with a burning taste and unpleasant odour; easily soluble in water and alcohol, yielding a strongly alkaline liquid; insoluble in ether.

Two series of crystalline salts were obtained; the following have been prepared: $C_5H_{12}N_2O_2.1\frac{1}{2}HCl$: $C_5H_{12}N_2O_2.HCl$: $2C_5H_{12}N_2O_2.1\frac{1}{2}\overline{Ox}$.

The second and third were prepared from the first, which was itself obtained by boiling ornithuric acid with hydrochloric acid, filtering from separated benzoic acid, concentrating and treating with alcohol.

The formation of ornithuric acid is analogous to that of hippuric acid, this compound being derived from 2 molecules of benzoic acid, and one of the base $C_5H_{12}N_2O_2$, with elimination of 2 molecules of water:

$$2(C_7H_6O_2) + C_5H_{12}N_2O_2 = C_{19}H_{20}N_2O_4 + 2H_2O.$$

M. M. P. M.

Ornithuric Acid and its Derivatives. By M. JAFFE (*Deut. Chem. Ges. Ber.*, xi, 406—409).—Calcium and barium ornithurate are described: $Ca(C_{19}H_{19}N_2O_4)_2$, and $Ba(C_{19}H_{19}N_2O_4)_2$, respectively. The former is a crystalline salt, very slightly soluble in water, hot or cold, insoluble in alcohol and in ether. The latter forms a snow-white mass, easily soluble in water and in alcohol, insoluble in ether. The composition of these two salts shows that ornithuric acid is a monobasic acid, whilst the sparing solubility of the calcium salt and the ready solubility of the barium salt are very characteristic. For the base, $C_5H_{12}N_2O_2$, previously obtained by the author from birds' excrement, the name of *ornithine* is suggested.

By boiling ornithuric acid with hydrochloric acid until the whole is just dissolved, a product is obtained which the author calls *monobenzoylornithine*, $C_{12}H_{16}N_2O_3$, or $C_5H_8O_2.NH_2.NHC_7H_5O$. This body crystallises in hard, colourless needles, melting at 225—230°, easily soluble in water, but insoluble in alcohol and in ether.

Monobenzoylornithin forms easily soluble salts with mineral acids; by long-continued boiling with hydrochloric acid, it is decomposed into benzoic acid and ornithine. The formula formerly given for ornithine is confirmed by the preparation and analysis of the nitrate, which is a salt analogous in general properties to the chlorhydrate, crystallising in broad colourless plates. The author is inclined to regard this base as a diamido-derivative of a fatty acid, probably a diamidovaleric acid, $C_5H_8(NH_2)_2O_2$. M. M. P. M.

Action of Chlorine on Metachloracetanilide. By F. BEILSTEIN (*Deut. Chem. Ges. Ber.*, xi, 680).—The product of the above reaction is the compound $C_6Cl_5.OH.Cl_2$, which forms large crystals (m. p. 68·5—70°), soluble in alcohol, benzene, and carbon bisulphide.

C. F. C.

Action of Phosphorus Pentasulphide on Acid Amides. By A. BERNTHSEN (*Deut. Chem. Ges. Ber.*, xi, 503).—Thiamides can be conveniently prepared by the action of phosphorus pentasulphide on amides. *Benzothianilide* is obtained by gently warming a mixture of the pentasulphide with twice its weight of benzanilid. The syrupy mass is extracted with alcohol, caustic sodia is added, and the solution is poured into water. On the addition of hydrochloric acid, the benzothianilide is precipitated. In a similar way, *phenyl acetothiamide* can be prepared from phenylacetamide. W. C. W.

Remarks on Bernthsen's Paper "On the Action of Phosphorus Pentasulphide on Acid Amides." By A. W. HOFMANN (*Deut. Chem. Ges. Ber.*, xi, 504—507).—This is merely a reply to Bernthsen's complaint, that Hofmann was encroaching on his subject, and does not possess any scientific interest. W. C. W.

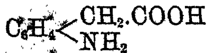
A New Chloride of Camphor (Preliminary Notice). By F. V. SPITZER (*Deut. Chem. Ges. Ber.*, xi, 363—364).—When finely-divided camphor is added gradually to phosphorus pentachloride, the whole being kept cool, a nearly pure dichloride of camphor is produced. It melts at 150—155°, whilst the isomeric dichloride obtained by Pfaundler melts at 70°. The author is making a complete investigation of this new substance. T. C.

Action of Boron Fluoride on Camphor. By F. LANDOLPH (*Compt. rend.*, lxxxvi, 539—541).—Camphor, heated to its melting point, absorbs boron fluoride, and combines with it in equivalent proportion, forming a compound which crystallises in slender prismatic needles melting at about 70°. When this was heated in a sealed tube for 24 hours at 250°, boric acid was produced, besides liquid and gaseous products, the chief of which were:—Cymene and its polymerides; hydrocarbons belonging to the acetylene series C_nH_{2n-2}; carbonic oxide; ethylene; and propylene. These results the author considers to point to the constitutional formula, $C_6H_4.H_2.CO(CH_3)(C_3H_7)$, for camphor, from which it appears that the generating hydrocarbon of camphor must be hexylene, C_6H_{10}; and consequently there is a possibility of forming camphor synthetically from hexylene. R. R.

Isatin and its Derivatives. By W. SUIDA (*Deut. Chem. Ges. Ber.*, xi, 584—587).—*Acetylisatin* prepared by heating isatin with twice its weight of acetic anhydride for 3—4 hours, crystallises in yellow prismatic needles, which melt at 141°. It dissolves readily in benzene and in alcohol, and splits up into isatin and acetic acid on boiling with water, or more easily with hydrochloric acid.

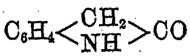
A dilute solution of potassium hydrate dissolves acetylisatin, and dilute sulphuric acid precipitates acetylisatic acid from this solution. Acetylisatic acid, $C_{10}H_9O_4N$, is a white crystalline substance (m. p. 160°), soluble in alcohol, ether, and benzene. It forms isatin when boiled with hydrochloric acid. By the action of sodium amalgam on an acetic acid solution of acetylisatic acid, *acetylhydrindic acid*, $C_{10}H_{11}NO_4$, is produced. This substance forms colourless, needle-shaped crystals (m. p. 142°), which dissolve freely in water, alcohol, chloroform, and glacial acetic acid, but are insoluble in petroleum ether. This acid does not yield isatin on boiling with hydrochloric acid. Reducing agents (hydriodic acid or sodium amalgam) split up acetylhydrindic acid, forming acetic acid and oxindol.

Since acetylhydrindic acid is formed from acetylisatic acid, by the direct addition of two atoms of hydrogen, it cannot be an aldehyde, but must be identical with acetyl-orthoamidomandelic acid, and therefore bears the same relation to di-oxindol that acetylisatic acid does to isatin. The constitution of these bodies may be represented by the following formulæ:—



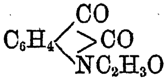
$$C_6H_4<\substack{CH_2.COOH\\NH_2}$$

Orthoamidomandelic acid.



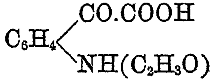
$$C_6H_4<\substack{CH_2\\NH}>CO$$

Oxindol.



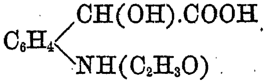
$C_6H_4\begin{matrix}CO\\ >CO\\ NC_2H_3O\end{matrix}$

Acetylisatin.



$C_6H_4\begin{matrix}CO.COOH\\ NH(C_2H_3O)\end{matrix}$

Acetylisatic acid.



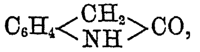
$C_6H_4\begin{matrix}CH(OH).COOH\\ NH(C_2H_3O)\end{matrix}$

Acetylhydrindic acid.

Acetyloxindol begins to sublime at 100°, and melts at 130°. By adding sulphuric acid to a solution of this compound in sodium hydrate, a new crystalline body is obtained, which will form the subject of further research. W. C. W.

Synthesis of Oxindol. By A. Baeyer (*Deut. Chem. Ges. Ber.*, xi, 582—584).—The product of the action of tin and hydrochloric acid on a mixture of isomeric nitrophenylacetic acids, is neutralised with marble, and boiled with precipitated barium carbonate. The para- and meta-amido acids form barium salts, but the ortho-acid remains in solution in the form of an anhydride, and can be extracted with ether. This anhydride of orthoamidophenylacetic acid is identical with oxindol. It yields indol on heating with zinc dust.

This result confirms the correctness of the formula,



$C_6H_4<\begin{matrix}CH_2\\ NH\end{matrix}>CO,$

for oxindol. W. C. W.

Methyl Derivatives of α-Naphthylamine. By L. Landshoff (*Deut. Chem. Ges. Ber.*, xi, 631—646).—It has already been shown (*Ber.*, x, 594 and 1582) that by the action of methyl chloride on aniline and toluidine, methyl substitution products of the respective bases are obtained. Its reaction with naphthylamine is somewhat different in character. By passing methyl chloride into naphthylamine at the temperature of 150—180°, the author obtained, in addition to a methyl derivative, dinaphthylamine; the latter results from the action of naphthylamine on the naphthylamine hydrochloride which is formed in the course of the reaction. In order to identify this compound, a comparison was made between it and dinaphthylamine prepared directly from naphthylamine and naphthylamine hydrochloride, by converting them both into nitrosodinaphthylamine, $(C_{10}H_7)_2(NO)N$. In both cases the nitroso compound was obtained as a yellow crystalline powder, melting at 260—262°, with decomposition. Monomethylnaphthylamine, $C_{10}H_7(CH_3)HN$ (b. p. 293°), was also isolated from the product of the reaction: the acetyl derivative of this compound, $C_{10}H_7(CH_3)(C_2H_5O)N$, crystallises in small white prisms, melting at 90—91°, easily soluble in alcohol and ether, but with difficulty in water. By the action of methyl iodide (2 mols.) upon naphthylamine (1 mol.) dissolved in methyl alcohol, in sealed tubes at 100°, dimethylnaphthylamine, $C_{10}H_7(CH_3)_2N$, is obtained as a bright yellow oil, with a green fluorescence, boiling at 267°.

By heating this compound with methyl iodide for some days at 100°, in sealed tubes, trimethylnaphthylammonium iodide, $C_{10}H_7(CH_3)_3I$, is formed. This body crystallises in large, yellow needles, which are soluble in water, yielding a green solution. At 164° it is resolved into methyl iodide and dimethylnaphthylamine. The corresponding hydroxide, obtained by the action of silver oxide, is a powerful base, forming well crystallised salts. C. F. C.

Formation of Xanthine Derivatives by the Action of Pancreas Ferment on Albumin. By G. SALOMON (*Deut. Chem. Ges. Ber.*, xi, 574—576).—Hypoxanthine is formed by the action of pancreas ferment on pure blood fibrin. It is also produced in much smaller quantities, in the absence of pancreas ferment, by simple decay. Schützenberger (*Bull. Soc. Chim.*, 1874) has shown that in the decomposition of the albuminous constituents of yeast, leucine, tyrosine, xanthine, hypoxanthine, guanine, and carnine are formed.

W. C. W.

Sulphate of Quinidine. By J. E. DE VRIJ (*Pharm. J. Trans.* [3], viii, 745).—Pure sulphate of quinidine contains 2 molecules of water, $2(C_{20}H_{24}N_2O_2).SO_4H_2 + 2H_2O$, as A. C. Oudemans has shown from the analysis of three different samples. The commercial sulphate, as Petit states, is, however, practically anhydrous, a sample analysed by the author containing only 0·35 per cent. water.

The purity of quinidine may be tested as follows:—By adding potassium iodide to a solution of the pure sulphate in 50 parts of water, a sandy crystalline precipitate is formed; and if, after leaving the liquid for some time, then filtering and adding ammonia, it remains clear, the salt may be regarded as pure; if the precipitate is resinous instead of sandy, cinchonine or cinchonidine, or perhaps both, are present; and if, after filtering and adding ammonia, only a slight turbidity is formed, the salt contains only traces of other cinchona alkaloïds, and is commercially pure. L. T. O'S.

Quiniretin. By F. A. FLÜCKIGER (*Pharm. J. Trans.* [3], viii, 885—886).—The action of light on quinine salts has been previously studied; and in order to ascertain whether the free base undergoes any change in sunlight, a clear solution of 1 part of quinine in 2,000 of water was exposed to direct sunshine in July and August, when it assumed a yellowish or brownish coloration, from which, after a few days, a flocculent brown precipitate separated, only a very small trace of alkaloïd being left in solution. The change takes place when quinine dissolved in water previously freed from air by boiling, is exposed to sunlight, also on exposing a solution of quinine to the direct rays of the sun in an atmosphere of hydrogen. The author therefore considers that this substance, which he calls *quiniretin*, must have the same composition as quinine. It has no alkaline reaction, nor does it neutralise acids, in which it is freely soluble; it has a very bitter taste, and is insoluble in alcohol, ether, and water. The hydrochloric acid solution is precipitated by ammonia, but not by tannin. Nessler's solution produces a precipitate. It is dissolved by chlorine-water, the solution yielding a green precipitate when treated with ammonia. Dry quinine is not so readily transformed as when it is dissolved in water or alcohol. The other cinchona alkaloïds being more sparingly soluble in water, are not so easily changed. Solutions of quinic acid, concentrated or dilute, are scarcely affected by exposure. Aqueous solutions of morphine or strychnine are only slightly coloured, whilst codeine and brucine are coloured very much. It seems that the solubility of the alkaloïd plays a prominent part in the transformation, but the subject requires further investigation.

L. T. O'S.

Veratrum Alkaloïds. By A. TOBIEN (*Pharm. J. Trans.* [3], viii, 808—810).—After a historical sketch and a detailed account of the extraction of the alkaloïds from *V. lobelianum*, which contains principally a mixture of jervine and veratroïdine, the author gives the following properties and reactions:—

1. Jervine obtained from the nitrate by treatment with sodium carbonate solution, and subsequent crystallisation from alcohol, forms colourless needles, having the formula $C_{13}H_{23}NO_4$, or more closely, $C_{27}H_{47}N_2O_8$, but the latter cannot be correct, since the total number of nitrogen and hydrogen atoms is not an even number. It is a monacid base, insoluble in petroleum spirit, sparingly soluble in water, alkaline carbonates, and ether, more so in amyl alcohol and benzene, and freely soluble in alcohol. It is dissolved by sulphuric acid, with a yellow colour, which gradually changes to green. Hydrochloride of jervine, when heated with nitric acid, gives a rose colour, but a mixture of the concentrated acids has no effect on the free base.

2. Veratroïdine is obtained from a solution in chloroform as a yellow amorphous mass, which, when treated with sulphuric acid, gives first a yellow solution, which changes to light brown, and finally to raspberry red. Concentrated hydrochloric acid gives a yellowish, rose-red coloration, which, on addition of sulphuric acid and heating, changes to brown-red.

Concentrated nitric acid dissolves veratroïdine with a light yellow colour, and on treatment with sulphuric acid and heating, it changes into an orange, and finally a lemon-yellow.

The presence of veratrine will modify these reactions, but it can easily be detected by the permanent red coloration produced by heating a solution of the alkaloïd in concentrated hydrochloric acid, which dissolves it in the cold without colour.

The ultimate analysis of veratroïdine indicates the formula,

$$C_{51}H_{78}N_2O_{16} \text{ or } C_{24}H_{37}NO_7.$$

In its physiological action it resembles veratrine. Veratrine when treated with sulphuric acid and sugar, gives a green colour.

The composition of the veratrum alkaloïds are, according to Weigelin and Tobien, as follows:—

Veratrine	$C_{52}H_{86}N_2O_{15}$, W.
Veratroïdine..........	$C_{51}H_{78}N_2O_{16}$ or $C_{24}H_{37}NO_7$, T.
Sabatrine	$C_{51}H_{86}N_2O_{17}$, W.
Sabadilline	$C_{41}H_{66}N_2O_{13}$, W.
Jervine	$C_{27}H_{47}N_2O_8$, T.?

L. T. O'S.

Alkaloïd of Duboisia Myoporoïdes. By A. W. GERRARD (*Pharm. J. Trans.* [3], viii, 787—790).—This alkaloïd is obtained by mixing an aqueous extract of the bark with an equal volume of water, and adding alcohol until no further precipitation takes place. The solution is filtered, and the alcohol distilled off; the residue is then diluted with water, treated with a slight excess of ammonia, and shaken with chloroform, which dissolves the alkaloïd. The solution in chloroform is evaporated, and the residue dissolved in dilute sulphuric acid, and neutralised with ammonia, when oily drops separate out, from which the alkaloïd is extracted by ether.

It is thus obtained as a yellow viscous mass, soluble in alcohol, chloroform, ether, benzene, and carbon bisulphide, but only sparingly soluble in water, to which it imparts an alkaline reaction. In its physiological, and also in some of its chemical actions, it resembles atropine.

With tannic acid and Nessler's solution it gives white precipitates, the former being soluble in hydrochloric acid; alkalis give white precipitates, soluble in excess; chlorides of platinum and gold produce yellow precipitates. Mercuric chloride precipitates concentrated solutions of the alkaloïd. Concentrated nitric acid gives with duboisine a slight brown coloration; but no reaction with atropine. Concentrated sulphuric acid in the cold has no action on atropine, but on heating, it darkens in colour, and evolves an aromatic odour, which is increased by the addition of potassium dichromate, chromic oxide being precipitated. Duboisine treated in a similar manner gives, in the cold, a reddish-brown colour, and on heating, an odour of butyric acid, whilst chromate of potash is not reduced.

When boiled with baryta-water, atropine evolves an odour, which, according to the author, resembles oil of gaultheria, but according to others, of hawthorn, whereas duboisine evolves an odour of butyric acid. The free alkaloïd is more soluble in water than atropine. The sulphate and hydrobromide are the only salts which crystallise. Its physiological actions resemble those of atropine. It dilates the pupil of the eye; causes dryness of the mouth, and thirst; it effectually prevents the action of muscarine on the heart, and after the lapse of some time produces tetanus.

The author proposes that it should be called duboisine, if after further research it should be found not to be identical with atropine.

L. T. O'S.

Products of Oxidation of Cholic Acid from Ox-bile and of the Acids derived from Cholesterine. By P. LATSCHINOFF (*Bull. Soc. Chim.* [2], xxxix, 212—213).—The author's results tend to prove that cholic and cholesteric acids are analogous, differing merely in their state of hydration. The products of oxidation of cholic acid and cholesteric acid are the same, and are formed almost in the same proportion; they consist of a small quantity of acetic acid, carbon dioxide, and the cholesteric acid, $C_8H_{10}O_5$, obtained by Redtenbacher as a product of the oxidation of bile. The author is of opinion that the formula for cholesteric acid ought to be $C_9H_{12}O_6$, or $C_9H_{10}O_8$, instead of $C_8H_{10}O_8$.

L. T. O'S.

The Colouring Matter of Birds' Egg-shells. By C. LIEBERMANN (*Deut. Chem. Ges. Ber.*, xi, 606—610).—The blue or green colour of birds'-eggs is due to a bile pigment, which resembles biliverdin in certain respects. The shells frequently contain a second colouring matter, not a bile pigment, which exhibits a characteristic absorption spectrum.

W. C. W.

Invertin. By M. BARTH (*Deut. Chem. Ges. Ber.*, xi, 474—482).

—Yeast dried at a temperature not exceeding 40°, is finely powdered and heated at 105° for 6 hours. It is then well mixed with water, and left at rest for 12 hours at 40°. The aqueous extract is rapidly filtered into five times its volume of alcohol of 95 per cent., and the precipitated invertin is collected on a filter, and washed with alcohol. This crude product, after being pressed between bibulous paper, to remove the alcohol, is digested with water. The invertin dissolves, leaving an insoluble residue of albuminous matter. The addition of alcohol to the solution precipitates pure invertin, which is washed with absolute alcohol and dried *in vacuo.* 500 grams of yeast yield about 2 grams of invertin in the form of a white powder, soluble in water.

If the precipitated invertin is washed with alcohol of 95 per cent., instead of absolute alcohol, it retains water, and when dried forms a brown, horny mass, not completely soluble in water. This modification is inactive, and is identical in its properties with the invertin described by Donath (*Ber.*, viii, 795), Gunning (*ibid.*, v, 821), and Berthelot.

A solution of invertin is neutral to litmus; it precipitates lead, copper, and mercurous salts, but has no action on ferric chloride or potassium ferrocyanide, and is not rendered turbid by boiling with acetic acid. Invertin does not yield leucine on treatment with sulphuric acid.

Both the brown and the white substances contain 22 per cent. of ash, which consists chiefly of phosphates of calcium, magnesium, and potassium.

The composition of these two bodies (after deducting the ash) is—

	C.	H.	N.	S.	O.
Brown	42·6	9·1	6·5	0·56	41·24
White........	43·9	8·4	6·0	0·63	41·17

Invertin is slower and more feeble in its action than other ferments. 5 milligrams of invertin can convert 3·8 grams of cane sugar into invert sugar in 48 hours. W. C. W.

On the Nuclein of Milk. By N. LUBAVIN (*Bull. Soc. Chim.* [2], xxxix, 213).—The nuclein of milk, according to the author, is not a phosphate of casein, but some other compound of phosphoric acid. It has the properties of a weak acid, and its lead salt, in which the relation of lead to phosphorus is as Pb_3 to P_2, is obtained as a granular precipitate when lead oxalate is added to a solution of nuclein in sodium acetate.

The casein precipitated from an alkaline solution by hydrochloric acid may be obtained in fractions containing different quantities of phosphorus. L. T. O'S.

Putrefaction of Elastin and Mucin. By G. WÄLCHLI (*J. pr. Chem.* [2], xvii, 71—78).—Elastin was prepared from the neck-band of oxen by a method analogous to that adopted for preparing cellulose, viz., by successive treatment with a mixture of alcohol and ether, acetic acid, potash solution, and, finally, washing the product with water. 100 grams were mixed with 4 litres of water and 5 grams ox pancreas, and maintained at 35° to 40° during 15 days. Deducting the amount of undecomposed elastin, it was found that 93 grams of this body yielded 1·74 grams ammonia, 8·15 grams valeric acid, 9·4 grams glycocol and leucin, besides carbon dioxide, and, as chief product, a syrupy peptone-like liquid. Elastin is thus shown to be analogous with glutin, and to belong to the proteïn compounds of the connective tissue.

Mucin was prepared by treating finely divided snails with hot water, precipitating the filtrate with acetic acid, and removing the fat by means of ether. The mucin was subjected to the action of pancreas at 35—40° until it was entirely dissolved: the main liquid product was a fetid oil: indol and phenol were produced, as also ammonia, butyric acid, and a substance which exerted a powerful reducing action on Fehling's solution. Unfortunately the whole of this sugar-like body was lost.

M. M. P. M.

On the Composition of Wool. By P. Schutzenberger (*Compt. rend.*, lxxxvi, 767—769).—The author finds that the decomposition of 100 grams of purified wool by an aqueous solution of barium hydrate (300—400 grams) at 170°, yields the following products:—

Nitrogen (evolved as ammonia)	5·25
Carbonic acid (separated as $BaCO_3$)	4·27
Oxalic ,, (separated as BaC_2O_4)	5·72
Acetic ,, (by distillation and titration)	3·2
Pyrrol and volatile products	1 to 1·5

Elementary composition of fixed residue, containing leucine, tyrosine, and other nitrogenous products	C	47·85
	H	7·69
	N	12·63
	O	31·83
		100·00

The author represents the decompositions by empirical formulæ.

C. F. C.

Physiological Chemistry.

Composition of the Food of Four Miners at the Silberau Mine, Ems. By E. Steinheil (*Zeitschr. f. Biologie*, xiii, 403—423).—The experiments were made on four days in June, 1877. The men work ten hours per day, and their ages and weights were:—

(1.)	31 years	68·25 kilos.
(2.)	22 ,,	62·30 ,,
(3.)	36 ,,	67·50 ,,
(4.)	23 ,,	67·50 ,,

The average daily consumption of food was found to be:—

	Grams.		Albumin.	Fat.	Carbohydrates.
Roasted coffee	12·35	=	—	—	—
Chicory	2·45	=	—	—	—
Lean meat	63·39	=	13·88	0·57	—
Fatty tissue in meat	12·25	=	—	11·71	—
Smoked bacon	42·95	=	0·73	40·59	—
Salt	13·07	=	—	—	—
Black bread	781·69	=	62·54	11·73	384·62
Butter	45·20	=	0·41	41·63	—
Potatoes, raw	274·00	=	5·48	0·82	59·73
„ steamed ..	240·30	=	4·81	0·72	52·39
White beans	62·50	=	15·31	1·25	34·85
Peas	42·19	=	9·50	1·06	24·56
Groats	31·25	=	3·53	—	21·81
Lentils	52·95	=	13·78	1·06	29·15
Wheat meal	3·12	=	0·37	0·04	2·30
Vinegar	8·50	=	—	—	—
Rice	31·25	=	2·34	0·09	24·41
Rape oil	1·85	=	—	1·85	—
		Total	132·68	113·12	633·82

G. T. A.

Distribution of Zinc in the Animal Body after Hypodermic Injection. By MATZKEWITSCH (*Deut. Chem. Ges. Ber.*, xi, 680).—100 parts of ZnO, in the form of acetate, being injected under the skin of a dog, it was found to be distributed over the several parts of the body in the following ratios:—Bones, 35·49; skin, 3·70; place of injection, 2·19; brain, 1·02; liver, 1·75; lungs and heart, 1·68; kidneys, bladder, and urine, 1·14; stomach and intestines, 4·13; muscles, 60·5. The previous absence of zinc was determined by experiments on normal animals. C. F. C.

Decomposition of Blood by "Bacillus subtilis." By C. KAUFMANN (*J. pr. Chem.* [2], xvii, 79—96).—Grossmann and Meyerhausen (*Pflüger's Archiv.*, xv, 245) have shown that bacteria are more active in oxygen than in ordinary air, but that they are killed by ozone. The experiments of the author, carried out with defibrinated blood (rabbits' and frogs') containing bacteria (chiefly *Bacillus subtilis*) and exposed to a constant stream of oxygen, show that at first the bacilli are very active, but that after a time they altogether cease to move about. The action of oxygen upon bacteria in presence of blood is, therefore, analogous to the action of ozone in absence of the same fluid. When the stream of oxygen was stopped, the bacteria gradually resumed their activity, and the blood particles became decomposed. Hæmoglobin remained undecomposed longer than the other constituents of the blood. M. M. P. M.

The Means whereby Acids are produced in the Organism. By R. MALY (*Chem. Centr.*, 1878, 56—63 and 73—80).—The author's principal results are as follows:—

1. Blood serum contains salts possessed of acid reaction, notwithstanding its alkaline reaction: monosodium phosphate especially is present in blood.

2. Some of the compounds contained in blood which exhibit alkaline reaction — more especially hydrogen-sodium carbonate, and disodium phosphate—are theoretically acid salts.

3. During oxidation processes the amount of acid in the blood increases.

4. The partition and mutual combinations of acids and bases in the blood are extremely complicated: free carbonic acid is always present, and this body decomposes many of the salts in blood, with production of free mineral acid.

5. Acid salts diffuse more rapidly and more completely than normal salts, and acids more readily than acid salts. The production of acid salts and of acids in the various liquids of the body is therefore greatly aided by diffusion, which takes place more perfectly in the organism than under any conditions that can be artificially attained.

Experiments are detailed proving the formation of free hydrochloric acid by the decomposition of mono- and di-sodium phosphate by sodium and calcium chlorides. M. M. P. M.

Action of Oxygen on Anatomic Elements. By P. BERT (*Compt. rend.*, lxxxvi, 546).—The paper refers to some experiments on the poisonous effects of oxygen on animals confined in compressed air. The general conclusions are that in the normal state oxygen does not exist in the state of simple solution either in the plasma or in the tissues, but that these derive it from the hæmoglobin, which, however, is never completely saturated with it. Under a pressure of 8 or 6 atmospheres, however, the colouring matter of the globules becomes completely saturated with oxygen, and the latter then begins to be dissolved in the plasma. When the tissues are caused to take up free oxygen, they cannot live at its expense, and even become incapable of absorbing it from the substances which would otherwise enable them to live. Some organic elements, such as the elements of animal tissues, butyric vibrios, yeast in a state of activity, &c., are able chemically to reduce matter external to themselves (hæmoglobin, lactic acid, glycose), whilst others, such as the red globules of the blood, live at the expense of material entering into their own substance. R. R.

Occurrence of Allantoïn and Hippuric Acid in Dog's Urine. By E. SALKOWSKI (*Deut. Chem. Ges. Ber.*, xi, 500—502).—Allantoïn is sometimes found in the urine of dogs which have been fed exclusively on animal food. An abnormally large amount of uric acid is generally found in those specimens of urine which do not contain allantoïn.

The urine of dogs fed exclusively on animal food is generally considered to contain little or no hippuric acid. The author finds, however, that such urine always contains it in small quantity. The proportion between the hippuric acid and the urea in the urine was not found to exceed 1 part of the former to 129 of the latter. The amount of hippuric acid excreted is not influenced by binding the intestines with a ligature. W. C. W.

Origin of Uric Acid in the Organism of Birds. By H. MEYER and M. JAFFE (*Deut. Chem. Ges. Ber.*, x, 193).—A note calling in question the results of v. Knieriem, viz., that the supply of such materials as glycocine, leucine, &c., to birds causes an increase in the amount of urea excreted. The whole subject, the authors admit, is in need of further investigation. M. M. P. M.

Chemistry of Vegetable Physiology and Agriculture.

The Chemical Composition and Functions of Leaves. By B. CORENWINDER (*Compt. rend.*, lxxxvi, 608—610).—Carbonic acid is evolved from young leaves during the day as well as during the night, and at the same time oxygen is taken up. This exhalation of carbonic acid diminishes as the leaves grow, and finally ceases during the day. Nitrogenous substances are found to be most abundant in the young leaves, and to diminish gradually as they grow, and the same holds good for the phosphoric acid, from which the author concludes that there is a proportional relation between the respiration and the predominance of nitrogenous substances.

Experiments made with *Cerasus Laurocerasus* gave the following results:—The young leaves yielded, when dried at 100°, per cent.—

	Young leaves.	Old leaves.
Nitrogenous matter	32·47	10·75
Total ash	5·55	7·56
Phosphoric acid (in ash)....	1·68	0·35
Lime (in ash)	0·86	3·80

The greater percentage of ash in the old leaves is due chiefly to an increase in lime. A microscopical examination of the young leaves showed a large quantity of protoplasm, and but little chlorophyll. This protoplasm is rich in nitrogen and phosphorus, and is the chief vital principle of the cells. The old leaves contained, however, large quantities of chlorophyll, and but little protoplasm. The respiration in them is feeble, and is masked by the chlorophyll retaining and decomposing the carbonic acid as it is evolved. This function of the chlorophyll cannot be looked upon as an act of respiration; it is simply one of assimilation.

The author regards the breathing of plants as absolutely the same as that of animals. There is no difference between the respiration of plants during the night and during the day, as has generally been supposed. R. C. W.

Ripening of Grapes removed from the Vine. By E. POLLACCI (*Gazzetta chimica italiana*, vii, 517—520).—As it was not known with certainty whether the process of ripening continued in sour grapes after separation from the vine, experiments were made with this object, by taking bunches of sour grapes, dividing them as equally as possible both as to the state of maturity, size, &c., of the grapes, and the weight, then estimating the glucose and the acid in one portion of the freshly-gathered grapes, and the same in another portion after the lapse of 10 or 12 days, the cut grapes being kept in the shade; in every instance the amount of glucose had increased, whilst that of the acid had diminished: this effect was still more marked when the fruit was exposed to sunshine. It is evident, therefore, that grapes gathered whilst unripe continue to ripen; this action, however, was found to cease after a time, so that the fruit never becomes fully ripe.

C. E. G.

Research on the Ripening of Olives. By A. ROUSSILLE (*Compt. rend.*, lxxxvi, 610—613).—The author gives the following analyses of the fruit and leaves of the olive, collected at intervals of one month, from the 30th of May to the 30th of November:—

Composition of the Leaves.	30th May.	30th June.	30th July.	30th Aug.	30th Sept.	30th Oct.	30th Nov.
Fat and chlorophyll ..	5·432	4·330	4·578	4·577	3·631	3·766	3·702
Nitrogenous substance	8·775	8·162	9·337	8·275	7·883	8·287	8·443
Lignin	18·886	16·444	18·833	20·778	27·709	27·514	28·117
Ash	7·777	7·217	6·987	8·091	6·610	6·848	5·861
Unestimated	59·130	63·847	60·265	58·279	54·207	53·585	53·877
Alkaline salts........	10·794	19·795	22·190	8·992	12·849	16·834	19·006
Earthy phosphates....	12·938	27·005	22·360	8·604	9·754	11·127	12·304
„ carbonates, &c.	70·554	49·820	46·410	75·606	72·483	69·009	65·740
Silica	5·714	3·380	9·040	6·798	4·918	3·030	2·950

Composition of the Pulp of the Fruit.	30th June.	30th July.	30th Aug.	30th Sept.	30th Oct.	15th Nov.
Water	22·003	60·690	66·051	56·005	51·688	50·198
Fat and chlorophyll	1·397	5·490	29·190	62·304	67·213	68·573
Nitrogenous substance ..	—	—	14·619	4·189	4·411	4·329
Lignin	—	—	13·341	7·432	7·072	6·096
Ash	—	—	4·156	2·736	2·964	3·060
Unestimated	98·603	94·510	38·694	23·339	18·340	17·940
Alkaline salts..........	—	—	81·818	82·500	86·353	85·916
Earthy phosphates, &c...	—	—	16·642	16·250	13·068	13·615
Silica	—	—	1·540	1·250	0·579	0·469
P_2O_5 in the alkaline salts	—	—	1·675	4·421	4·784	5·164

Fatty Matter and Chlorophyll.—The chlorophyll, which is very abundant in the leaves at the end of May, gradually diminishes in quantity; it does not migrate to the fruit.

Nitrogenous Matter.—In the leaves, the nitrogen increases until the end of July. In August it greatly diminishes, and accumulates in the pericarp of the fruit. A migration of nitrogen in the fruit then takes place, probably going to the endosperm, for the amount diminishes two-thirds by the end of September. Afterwards (when the kernel should be forming) the proportion slightly increases in both leaves and fruit.

Lignin.—In the leaves, this substance decreases in June, after which it continues to augment.

Mineral Matter.—In the leaves, the mineral matter increases to the end of August, and then diminishes until the fruit ripens. The proportion of alkaline salts increases until the end of July: in August it goes to the fruit, forming the chief mineral constituent. A steady increase in the leaves again takes place, and continues until the fruit is gathered. Magnesium and calcium phosphates augment in the leaves until July, rapidly diminishing in August, as is the case with the alkaline salts. It appears that the migration of the phosphates precedes that of the alkalis, corresponding with the migration of the nitrogenous matter; whereas that of the alkaline salts corresponds with the non-isolated proximate principles, and with their conversion into fatty substance. In the fruit, the mineral matter reaches its maximum by the end of August, and then diminishes, but again gradually increases as it ripens. The alkaline salts increase with the fatty matter in almost a definite proportion with the potassium phosphate, thus (combined with potassium):—

1·675	P_2O_5	at the end of August	with 29·190 fat.
4·421	,,	,, ,, September	,, 62·304 ,,
4·784	,,	,, ,, October	,, 67·213 ,,
5·164	,,	when the fruit was gathered	,, 68·575 ,,

The calcium and magnesium phosphate is at its maximum in August, at the same time as the nitrogenous matter. Phosphoric acid can enter the endosperm only in the form of alkaline phosphate.

Silica.—This substance was probably an accidental impurity.

The above experiments were made upon the "Blanquet" variety of the olive. R. C. W.

Nitrification by Organised Ferments. By SCHLOESING and MÜNTZ (*Compt. rend.*, lxxxvi, 892—895).—For the preceding communication on this research, see page 163 of this volume. Pasteur has shown that moulds and mycoderms are active agents in the oxidation of organic matter; the authors sought to ascertain whether these organisms have the power of oxidising nitrogen, as well as carbon and hydrogen. They experimented with *Penicillium glaucum*, *Aspergillus niger*, *Mucor mucedo* and *racemosus*, and *Mycoderma vini* and *aceti*. These fungi were grown in various media supplying ammonia or organic nitrogen, the conditions selected being suitable to nitrification. Nitric acid was not produced in any case. Instead of oxidising nitrogen, these low organisms feed on nitric acid and ammonia, and rapidly convert their nitrogen into organic substance. When both nitric acid and ammonia are abundantly supplied, the ammonia is assimilated in greater proportion than the nitric acid. According to early observations the presence of mould in nitre beds is prejudicial to the formation of saltpetre. There is apparently no loss of nitrogen during the growth of mould till fructification commences; rapid combustion of organic matter then takes place, and free nitrogen is evolved; at this stage ammonia also may be produced. Moulds and mycoderms thus tend to diminish the quantity of combined nitrogen existing on the globe.

It would seem, therefore, that nitrification is not brought about by the organisms generally recognised as active oxidisers of organic matter, but is the work of some particular body demanding further study. R. W.

The Absorptive Power of Soil. By J. M. VAN BEMMELEN (*Landw. Versuchs. Stat.*, xxi, 135—191).—The conclusions of other investigators previous to those arrived at by the author are briefly as follows:—

A. *Absorption-phenomena in Soils.*—(1.) The absorptive power is peculiar to cultivated soil (Knop, *Kreislauf des Stoffes*, 1868, 502).

(2.) Soils which are rich in silicates soluble in hydrochloric acid have the greatest absorptive power.

(3.) Potassium is absorbed most readily, then ammonium, magnesium, sodium, and calcium in progression.

(4.) NH_3, KHO, NaHO, $Ca(HO)_2$ are more readily absorbed than their salts, without at the same time an equivalent exchange of base and acid (Way, 1850, Heiden, Brutslein, *Jahresb. Agr.*, 1859, 1). The alkaline carbonates and phosphates are more readily absorbed than the other salts, whilst with the chlorides, sulphates, and nitrates of the alkalis and alkaline earths, the absorption consists in an equivalent exchange of metal only.

(5.) The exchange with the salts, or the complete absorption of the salt from its solution, is only partial, and depends (*a*) on the concentration of the solution; (*b*) on the proportions of the soil and solution; (*c*) on the composition of the salt; (*d*) on the temperature. The absorption is never simply proportionate to the increased strength of the solution or the increased amount of the soil, but it increases in a smaller proportion. With solutions containing 50 to 500 miligram-equivalents of a salt to the litre, 400 grams of soil exert an absorption which may be expressed by the formula $a' = a\sqrt{n}$, a and a' being the amounts absorbed, and n the state of concentration of two solutions (Bädeker, *J. f. Landw.*, vii, 48; Rautenberg, vii, 442).

(6.) The absorbed salt or basic oxide is but very slightly soluble in pure water, more soluble in water containing carbonic acid, but most soluble in hydrochloric acid.

(7.) The absorbed oxide can be re-exchanged by treating the soil with the solution of a salt of another metal.

(8.) Absorption with exchange of base must be ascribed to the presence of zeolitic silicates in the soil, for the following reasons:—(*a*) The double decomposition is closely connected with the metamorphosis of the soil-rocks (*Erdgesteinen*). (*b.*) Zeolites exhibit the same metamorphism when they are strongly shaken with saline solutions. The absorbed ammonia can be driven out only at a red heat, or by a solution of potash. (*c.*) Silicates in which the alumina is only slightly soluble absorb but a small amount of ammonia in exchange for lime, soda, and potash (Eichorn, *Jahresb. Agr.*, 1859, ii, 16). (*d.*) Soils which are rich in soluble silicates are generally strongly absorptive (Rautenberg, *J. f. Landw.*, 1862, vii, 49—67; Heiden, *Pr. Ann. d. Landw.*, xliii, 310). (*e.*) Ferric hydrate and aluminium hydrate absorb a slight amount of ammonia and potash, but no salts (Rautenberg, *J. f. Landw.*, 1862, vii, 422).

B. *Destruction of the Absorptive Power of Soils.*—When a decomposition of the basic zeolitic silicates takes place in the soil, the power of absorption of salts ceases, but it is restored if the soil be treated with a solution of sodium carbonate or calcium carbonate, or by boiling it with a solution of calcium chloride or sulphate. Hydrochloric acid destroys the absorptive power of soils, or diminishes it (Brustlein, *Ann. Chem. Phys.* [3], lvi, 157, 1859; Peters, *Landw. Vers. Stat.*, 1860, pp. 2, 145; Rautenberg, *J. f. Landw.*, 1862, viii, 438).

C. *Restoration of the Absorptive Power of Soils.*—As stated in the previous paragraph, the absorptive power of a soil is completely restored by a solution of calcium carbonate or sodium carbonate. Peters states that solutions of simple salts undergo double decomposition in large quantity when in contact with a porous soil, and that one of the newly-formed salts is retained in the soil. Assuming this to be correct, the absorption of potassium in a soil (restored to its normal power of absorption by treatment with calcium carbonate) may be accounted for. The same author also partially restored the absorptive power of a soil by treating it with a solution of calcium chloride and gypsum.

D. *Influence of Humus-substance upon the Power of Absorption in Soils.*—Turf and humic acid have the property of absorbing salts in a high degree (Heiden, *Jahresb. Agr. Chem.*, 1866, 27), as will be seen from the following experiment by Heiden, viz., 100 grams of humic acid (prepared from peat) were treated with solutions of potassium chloride and ammonium chloride, containing respectively 11 equiv. K, and 9½ equiv. NH_3, and the results were:—

(*a.*) Absorbed KCl = 5·2 equiv.
" NH_4Cl = 3·8 "
(*b.*) Absorbed with exchange of metal = 0·6 K equiv.
" " " = 0·4 NH_4 "

Rautenberg treated natural humus obtained from a hollow tree (containing 17·69 per cent. of mineral constituents, of which 0·67 per cent. was soluble in HCl) as follows: 25 grams of humus were neutralised with lime-water, and treated with 300 cc. of a solution of NH_4Cl containing 300 equivalents, when it was found that 5 equivalents of NH_3 were absorbed. Further, the amounts of Ca and Mg found in solution were respectively 3·7 and 2 equivalents, making 5·7 equivalents. Hydrochloric acid destroys the absorptive power of humus in great part.

Investigations by J. M. van Bemmelen.—The author chose for his investigations a heavy soil (taken 1 meter below the surface), free from carbonic acid, and poor in soluble salts and vegetable matter. An analysis of this soil resulted as follows, viz.:—

	CaO.	MgO.	K_2O.	Na_2O.	Fe_2O_3.	Al_2O_3.	P_2O_5.
1. Soluble in dilute acetic acid	0·09	0·09	0·22	0·27	trace	trace	0·008
2. Soluble in strong boiling HCl ...	0·39	1·47	0·97	0·06	7·15	6·35	0·107
3. Insoluble	0·12	0·34	2·05	1·48	1·55	5·87	—
4. Total..........	0·60	1·90	3·24	1·81	8·70	12·22	0·115

	SO_3.	Cl.	SiO_2.	H_2O at 100°.	H_2O at 100–200°.	Loss on ignition.
1. Soluble in dilute acetic acid	0·02	0·03	trace	—	—	—
2. Soluble in strong boiling HCl ..	—	—	—	—	—	—
3. Insoluble	—	—	—	—	—	—
4. Total	0·02	0·03	60·42	5·59	1·05	4·15=99·85

The amounts in line 3 were obtained by deducting the sum of those in lines 1 and 2 from line 4. From the above analysis it will be seen that this soil contains only traces of soluble sulphates and chlorides. The zeolitic constituents are present in large amount, but the amount of humus substance is not great.

The Power of Absorption of the Experimental "Soil A" for Potassium Chloride Solution.—The absorption experiments were carried out with every precaution, and the estimations of the different bodies present were very exact. It was found that the soil took up the potassium of the potassium chloride solution in exchange for sodium, calcium, and magnesium, whilst the chloride in the solution had not diminished in amount from that present in the potassium chloride solution originally taken for the experiment. The absorptions for all the following experiments were ascertained in the following manner:—50 or 100 grams of the soil were placed in stoppered flasks, covered with from 100 c.c. to 200 c.c. (in some experiments 125 to 250 c.c.) KCl solution, and allowed to remain thus for at least 24 hours, being, however repeatedly shaken up. The solutions were then filtered through dry filter paper, and the funnel and receiver for the filtrate were covered by a bell-jar closed with water, the funnel being further covered with a wet cover-glass in order to insure that concentration of the liquid should not occur during filtration.

The Power of Absorption of the Experimental Soil for Potassium Chloride Solution, after Exhaustion with Hydrochloric Acid ("Soil B").—For these experiments the soil was treated in the following manner, viz.:—A portion of the "soil A" was boiled with a large excess of concentrated hydrochloric acid and washed on a filter-paper with water until the washings appeared cloudy. As the same portion of soil was repeatedly used for these absorption experiments, and repeatedly boiled out with the acid, it was necessary to guard against loss of the most finely divided clay particles; and in order to do this, the finely divided suspended particles were allowed to settle down in the acid liquid, filtered off, and again added to the residue. A considerable amount of silicate is dissolved out of the soil by the foregoing process, but it was found that even after five boilings with hydrochloric acid, alumina was still dissolved out, proving that the soluble and insoluble silicates cannot be completely separated in this way. After the above treatment, the washed soil always exhibits an acid reaction, even after being left for days in water, and washed repeatedly by decantation (the washings being also acid). This acidity is due to the presence of basic aluminium chloride. The soil possesses only a very slight power of equivalent absorption for potassium chloride after exhaustion with hydrochloric acid, viz., 0·5 equivalent, this amount being doubtless absorbed by the still undecomposed zeolitic constituents of the soil. The reason why Heiden observed so little change in the absorptions was that he used more dilute solutions than van Bemmelen, and did not thoroughly boil the soil with *concentrated* hydrochloric acid. The soil exhausted with hydrochloric acid was used in the following absorption experiments, and for convenience will be called "Soil B."

Absorption Experiments with "Soil B" after Treatment with Calcium Chloride Solution.—The author obtained results similar to those of Peters: for on boiling the "soil B" with a neutral 10 per cent. calcium chloride solution, and washing it out well, an absorption of 1—3 equivalents of potassium was observed on treating the soil with the potassium chloride solution. In solution were obtained 1·06 equivalents of Ca, Na, Mg, 0·8 equivalent being Ca; whilst there was only a very slight trace of Al_2O_3. Water dissolves only a trace of Ca, Al, and Cl; in order, therefore, to account for the solution of the above-mentioned bodies, it must be assumed that there has been a double decomposition between the KCl and an insoluble or probably absorbed calcium compound. Most likely one of the following reactions occurred, viz.:—

1. Basic aluminium chloride formed with the $CaCl_2$ soluble double chloride of aluminium and calcium, and insoluble calcium aluminate.

2. Aluminium silicate or silicic acid and basic aluminium chloride formed with the $CaCl_2$, soluble double chloride of aluminium and calcium, and insoluble calcium silicate; the latter substance, or calcium aluminate, on being treated with KCl, then formed potassium aluminate or silicate and $CaCl_2$. The potassium carbonate in either case would be *physically* absorbed. Of course a portion of the potassium in the potassium compound might be brought into solution in exchange for calcium on treating it with $CaCl_2$ solution, but the probability is in favour of the opposite reaction occurring, as the author observed (1) that calcium chloride solution dissolved a slight amount of alumina out of the "soil B," and (2) potassium chloride solution exerted a similar action upon the basic aluminium chloride in "soil B," potassium being absorbed in equivalent amount to the aluminium which passed into solution. From the above experiments it appears that a

solution of calcium chloride slightly restores the absorptive power of a soil.

"*Soil B" treated with Calcium Carbonate.*—The absorption experiments after the calcium carbonate treatment, showed that potassium was exchanged for calcium, and, further, that calcium carbonate dissolved in the potassium chloride solution. Taking the amount of potassium absorbed by the soil itself to be 0·5 equivalent, it was found that 2·5 to 3 equivalents more potassium were absorbed and exchanged for calcium; the basic aluminium chloride also was decomposed and calcium chloride formed. The amount of calcium carbonate which dissolved in the potassium chloride solution depended upon the strength of the latter, as 100 c.c. KCl solution (containing 4 equivalents KCl) dissolved 15 mgr. $CaCO_3$; whilst 100 c.c. KCl solution (containing 20 equivalents KCl) dissolved 50 mgr. $CaCO_3$. The author considers that there is no restoration of the chemical absorptive powers in this instance, as there can be no formation of a calcium silicate, but only a double decomposition between the $CaCO_3$ and the KCl to a certain extent. The author's results coincide with those obtained by Peters, Brustlein, and Rautenberg.

"*Soil B" Treated with Caustic Alkalis and Alkaline Carbonates.*—On boiling the "soil B" with a strong solution of sodium carbonate, washing the residue well, and then treating it with potassium chloride solution, an absorption of potassium was observed equal to that exerted by the original soil. In another series of experiments it was found that the "soil B" strongly absorbed caustic potash without there being at the same time an equivalent exchange of the other constituents. The filtrates were all alkaline, and contained humus-substance in solution. Another series of experiments showed that the same "soil B" also absorbed considerable quantities of the carbonates of potassium and sodium, with only a very slight exchange of constituents. The author concluded, therefore, that a hydrated silicic acid present in the soil exerted an absorptive power upon solutions of the above-mentioned metals, and some direct experiments proved this to be the case. For instance, "1 gram of pure silicic acid dried at 100° and treated with 100 c.c. of potassium carbonate solution (containing 10·1 equivalents K) absorbed 9·9 equivalents K, whilst a very slight trace of silicic acid was found dissolved in the filtrate." Alumina was found to possess only a very trifling absorptive power for alkalis. The hydrated silicic acid in the "soil B" was derived from the silicates originally present in that soil, and was separated from them by the action of the hydrochloric acid. Mulder found that porous substances such as sand, pumice, &c., on being exhausted with hydrochloric acid, washed out and ignited, exerted a slight absorptive power upon alkaline solutions, especially carbonates; an observation which goes to prove the correctness of the conclusions arrived at by van Bemmelen. It was found that the "soil B" on being treated first with calcium carbonate, and then with potassium chloride solution, exerted a less absorptive power upon alkaline carbonates than if it had been first treated with a solution of sodium carbonate. In the first case calcium chloride would form and pass into the solution, and react upon the alkaline carbonates, thus impeding the absorptive power of the soil.

The experiments of A. Salomon (*Land. Versuchs. Stat.*, ix, 351) may perhaps be explained in the following way:—He found that kaolin, brick-clay, &c., absorbed calcium oxide when treated with solutions of calcium nitrate and ammonia; the amounts absorbed being in proportion to the state of concentration of the solution, and the amount of ammonia present; increasing in fact with the quantity of the latter. A calcium salt exerts only a slight absorptive power in a soil, as calcium replaces the other metals (present in the zeolitic silicates) in a smaller amount than potassium. If, however, ammonia be present in the solution of calcium nitrate, a certain amount of calcium hydrate and ammonium nitrate is formed, thus causing a disturbance of the equilibrium previously existing in the solution, owing to the absorption of the calcium oxide by the soil without an equivalent exchange of metal. This double decomposition may proceed until equilibrium is restored between the amounts of calcium oxide and ammonia absorbed, and the amounts of calcium nitrate, ammonia, calcium oxide and ammonium nitrate which have passed into solution. The absorption of the calcium oxide is a *physical absorption*, for it was found that hydrate of alumina, hydrated ferric oxide, and hydrated silicic acid absorbed all the calcium oxide out of a solution of that substance, as will be seen from the results of the following experiments:—

(1.) 1·5 grams of hydrated silicic acid dried at 100° absorbed out of 100 c.c. of a solution of calcium oxide (containing 2·63 equivalents) 2·39 equivalents.

(2.) 2 grams of hydrate of alumina (dried in air) absorbed out of 100 c.c. of the above-mentioned calcium oxide solution 2·33 equivalents.

Conclusions.—(1.) The absorption of the chlorides, nitrates, and sulphates of the alkalis and alkaline earths by a soil is induced by the presence of basic zeolitic silicates in the latter, which contain lime, soda, magnesia, and potash, and are soluble in hydrochloric acid. These oxides replace those of the saline solutions: firstly, those containing lime and soda; secondly, magnesia, and, least of all, potash. The amount of oxide absorbed depends upon the composition of the soil, the concentration of the solution, the ratio of the amounts of the soil and solution taken, and the temperature.

(2.) A soil absorbs the hydrates, carbonates, and phosphates of the alkalis and the hydrates of the alkaline earths in a greater degree than the potash out of the chlorides, nitrates, and sulphates of that metal. It is probable that an absorption occurs without an equivalent exchange of metal.

(3.) If a soil be exhausted with boiling hydrochloric acid, so that only the acid insoluble silicates, quartz grains, silicic acid, and humus residue remain, the absorption of the oxides from solutions of the alkalis and alkaline earths is reduced to a minimum.

(4.) Soil which has been exhausted with hydrochloric acid still possesses a strong absorptive power for the alkaline carbonates and hydrates, and for the soluble hydrates of the alkaline earths. This absorption takes place without a simultaneous exchange of metal, and the amount absorbed depends upon the strength of the solution and the ratio between the amounts of the solution and earth taken. It is not certain whether both alumina and silicic acid cause this absorption, but the latter undoubtedly plays an important part in it.

(5.) When a soil has lost its absorptive power for the chlorides, nitrates, and sulphates of the alkalis (with double decomposition between them and the alkaline earths) through exhaustion with boiling hydrochloric acid, it cannot be restored by treating it with solutions of sodium carbonate, calcium carbonate, or calcium chloride.

(6.) The absorption of potassium observed on treating the exhausted soil already mentioned, with a solution of sodium carbonate or calcium carbonate, is of the same nature as that described above (4) viz., "a formation of four salts takes place, but the alkaline carbonate is absorbed by the soil as soon as formed (without an equivalent exchange of metal); and this formation and absorption continues until equilibrium is restored between the absorptive power of the soil, the solvent power of the water for the salts, and the affinities existing between the salts themselves."

When calcium carbonate and potassium chloride are present together, there is less absorption of alkaline carbonate than when calcium carbonate and solutions of potassium or sodium carbonate are present together, owing to the calcium chloride formed exerting a resistance to the absorptive affinity of the soil for the alkaline carbonate.

The author appends to his work four tables, giving the numerical results obtained in his experiments. C. A. B.

Fertility of Volcanic Soils. By TRUCHOT (*Ann. Chim. Phys.* [5], xiii, 264—271).—Volcanic soils are generally remarkable for their great fertility. Pietro Gavazzi published a research on the analysis and fertilising power of lavas, &c. (*ibid.* [5], xi, 244, and this *Journal*, 1877, ii, 861), but no estimation of phosphoric acid is given, although it is one of the most important ingredients in a soil. Gasparin classifies soils according to the amount of phosphoric acid they contain. The author has made analyses of various rocks and the soils produced from them. The means of his determinations are the following:—

	Lime.	Potash.	Phosphoric acid.
Granite rocks	0·046	0·288	0·033
Volcanic „ (trachyte) ..	2·201	3·775	0·131
„ „ (lava)	8·120	1·427	0·880

The soils produced from the above vary greatly in their fertility. The granite is the worst; the lava the best, thus proving that the difference is due to the phosphoric acid and not to the potash. Although the granite, for instance, is poor in lime, still the addition of lime without phosphates does not increase its productive powers. The soils had the following composition:—

	Lime.	Potash.	Phosphoric acid.	Nitrogen.	Organic carbon.
[illegible] soil........	traces	0·290	0·066	0·101	1·358
[illegible] soil (lava).	2·333	0·218	0·305	0·197	1·805
[illegible]	7·387	0·417	0·339	0·260	1·304

R. C. W.

Analytical Chemistry.

Determination of Carbon Dioxide in Air. By W. HESSE (*Zetschr. f. Biologie*, xiii, 395).—The author's method is a modification of Pettenkofer's. A flask of known capacity is filled with the air to be examined, 10 c.c. of a solution of barium hydrate are added, the flask is shaken, and a drop of a solution of rosolic acid introduced; a doubly perforated cork, carrying in one hole a burette filled with a solution of oxalic acid, is next fixed in the neck of the flask, and the acid is allowed to flow in until the excess of baryta is neutralised, as is indicated by the disappearance of the colour.

The burette is provided with a stop-cock, and is drawn out to a point.

The barium solution is made of such a strength that 10 c.c. correspond with 30 c.c. of the solution of oxalic acid. The oxalic acid solution is made by dissolving 0·28636 gram of pure crystallised acid in a litre of water: 1 c.c. of this solution corresponds with 0·1 mgm. of carbon dioxide. G. T. A.

Estimation of Nitrogen Compounds in Oil of Vitriol. By G. E. DAVIS (*Chem. News*, xxxvii, 155).—The author shows in this paper that it is impossible to estimate with certainty the amount of nitrogen compounds in ordinary pyrites-vitriol by the oxidation methods, hitherto mostly employed in works, since the presence of arsenious acid must have a deoxidising action on the standard solutions used. The following method is very simple in application, and is not affected by any impurity likely to be present in ordinary oil of vitriol: 1 c.c. of the vitriol is measured very accurately by means of a fine pipette and introduced into Frankland's stop-cock tube, standing over mercury. The vitriol is allowed to run in, and the cup washed out with pure strong sulphuric acid. The bottom is now closed with the thumb, and the vitriol agitated with the mercury in such a way that an unbroken column of mercury always remains between the vitriol and the thumb. After five minutes the mercury is levelled and the volume of gas read off. For very accurate determination it is better to leave the tube to itself for several hours, and to note temperature and pressure, making the necessary corrections. The mercury reduces the whole of the nitrogen oxides to nitric oxide, and the presence of any other compound found in vitriol has no influence on this test. The only precaution to be taken is to have the vitriol in the tube strong enough. D. B.

Estimation of Nitrous Acid by means of Metadiamidobenzene. By P. GRIESS (*Deut. Chem. Ges. Ber.*, xi, 624—627).—The author finds that metaphenylenediamine (m. p. 63°) may with advantage be substituted for diamidobenzoic acid as a reagent for the detection and estimation of nitrous acid (*Annalen*, cliv, 333), not only as more easily to be obtained, but as being even more delicate; by this reagent the presence of 1 pt. nitrous acid in 10,000,000 pts. water may be detected with certainty. It is employed in the form of a solution in dilute sulphuric acid, which may be decolorised, if necessary, previously to use by treatment with animal charcoal. This reagent is unaffected by hydrogen peroxide, and many other oxidising agents which liberate iodine from potassium iodide. The means of discrimination thus afforded has enabled the author to disprove the statement of Meissner, that the action of the saliva on potassium iodide and starch paper is due to the presence of hydrogen peroxide, and to corroborate Schönbein in referring it to ammonium nitrite. The use of this reagent will be especially valuable in water analysis. The development of the yellow colour with nitrous acid is due to the formation of triamidoazobenzene, according to the equation—

$$2C_6H_8N_2 + HNO_2 = C_{12}H_{13}N_5 + 2H_2O.$$

C. F. C.

Estimation of Nitrous Acid. By C. Preusse and F. Tiemann (*Deut. Chem. Ges. Ber.*, xi, 627—637).—This paper contains the details of the process for the estimation of nitrous acid by means of metaphenylenediamine, as recently proposed by Griess. The standard solutions required are (1) a solution of 5 grams of the base in 1 litre of water, and slightly supersaturated with sulphuric acid; (2) a dilute sulphuric acid, 1 vol. acid to 2 vols. water; (3) a solution of pure potassium nitrite (prepared from $AgNO_2$ and KCl), containing 0·01 Mgr N_2O_3 in 1 c.c. The method consists in the observation of the depth of the colour developed in 100 c.c. of the solution under examination, on the addition of 1 c.c. of each of the above solutions of sulphuric acid and phenylenediamine: a comparative observation being made with the standard nitrite, exactly as in Nessler's ammonia test. As in this case also, the colour should not exceed a bright yellow; and in order to obtain correct results, precisely the same time (20—25 minutes) must be allowed for the development of the colour in comparative trials. The authors have established, by experiment, the following advantages of this over the zinc iodide and starch method:—(*a.*) It is unaffected by the presence of ferric salts, to the extent of 1—2 pts. in 100,000 of water, if sulphuric acid be likewise present. (*b.*) The development of the colour is not retarded nor otherwise influenced by the presence of organic matter; provided, of course, that this imparts no colour to the original solution. (*c.*) The presence of acetic acid does not interfere with the reaction, but even renders it more delicate. (*d.*) The solution of phenylenediamine is permanent. In order to estimate nitrous acid in waters coloured by impurities, these must be previously removed, either by the addition of a small quantity of a solution of sodium hydrate and carbonate, in which case the precipitate of earthy carbonate is frequently capable of decolorising the water, or in the case of soft waters, of a few drops of a dilute solution of alum, the precipitate of alumina exerting a similar action. If these fail, the method is no longer applicable. C. F. C.

Separation of Glucinum. By C. Rössler (*Zeitschr. Anal. Chem.*, 1878, 148—151).—If to a solution of a glucinum salt, ammonium phosphate be added in excess, the precipitate redissolved in hydrochloric acid, and the solution carefully neutralised by ammonia, added in successive small portions, and warming after each addition, glucinum-ammonium phosphate is precipitated in a permanently crystalline form. The author finds that this body is not the phosphate, $BeNH_4PO_4.H_2O$, as it contains 11·42 per cent. NH_4, and gives on ignition 76·10 per cent. BeP_2O_7, whereas the latter formula would require 12·83 per cent. NH_4, and 68·62 per cent. BeP_2O_7.

The author describes a method for the separation of glucinum from aluminium in cases where the latter is present in relatively large quantity. This consists in heating the solution of the mixed chlorides with potassium sulphate, the quantity of which should be about 12 times that of the alumina present, in sealed tubes at 180°, for about half an hour. The greater part of the aluminium is hereby separated in the form of the insoluble basic double sulphate (Mitscherlich, *J. pr. Chem.*, 83, 455). The small quantity of aluminium left in the filtrate from this compound may be eliminated by the usual method, *i.e.*, by precipitating the glucinum with ammonium phosphate, in presence of citric acid, in the form of the glucinum-ammonium phosphate previously described. C. F. C.

Volumetric Determinations by Chromic Acid. By C. W. HINMAN (*Amer. J. of Sci.* [3], xiv, 478—481).—Iodine liberated from iodides by chromic acid, enters into combination again when the acid is reduced, upon which fact the author bases the following methods for volumetric analysis. The reducing agent used is stannous chloride.

(1.) *Estimation of Chromic Acid.*—The chromate is weighed in a flask, which is filled nearly to the neck with water, and boiled to expel the air. When cold a small quantity of hydrochloric acid is added, and a solution of stannous chloride run in until the chromic acid is nearly but not entirely reduced. A few drops of starch-paste and potassium iodide are then introduced, and stannous chloride cautiously added, until the blue colour of the iodide of starch disappears. Lead, bismuth, and barium chromates may be determined by this method, the two former in an acetic acid solution, the latter in an ammoniacal solution. Of course bodies such as cupric and ferric salts, which reduce stannous chloride, must be absent, and the solutions must be sufficiently dilute to allow the blue colour of the starch test to be distinctly observed.

(2.) *Estimation of Lead.*—The estimation of lead is carried out as follows:—The salt of lead is dissolved in water, and a little acetic acid and excess of a standard chromate solution (containing 14·761 grams of potassium dichromate per litre) is added. The chromate of lead is filtered off, and the excess of chromate determined as above.

Arsenious and antimonious acids may also be determined by oxidising them with the dichromate, and then determining the excess of the latter.

(3.) *Estimation of Sulphuric Acid.*—To a slightly acid solution of a sulphate, excess of barium chromate is added, and the solution neutralised; the mixture of barium sulphate and chromate is filtered, and the chromic acid in the filtrate (which is equivalent to the sulphuric acid employed) is determined.

The author gives the following modification of the method for estimating iron by means of stannous chloride, as a simplification of the process given in the last edition of Fresenius' analysis. A small quantity of iodine, equal to one-fourth of a c.c. of the stannous chloride solution, is added to the decolorised iron, and when cold a little starch paste and stannous chloride, until the blue colour disappears. By subtracting the equivalent in stannous chloride of the iodine from the total amount of stannous chloride used, the quantity required by the iron is obtained.

The strength of the stannous chloride solution is not stated.

L. T. O'S.

New Method of Separating Arsenic from other Metals. By P. DE CLERMONT and FROMMEL (*Compt. rend.*, lxxxvi, 828—830).—On boiling with water sulphide of arsenic is resolved into sulphuretted hydrogen and arsenious acid; the solubility of the latter in water is made the basis of a separation of arsenic from those metals whose sulphides are similarly decomposed, but with formation of insoluble oxides. The method consists in boiling the mixed precipitates of sulphides, after washing, in a retort, the decomposition being much more rapid in this case than when the boiling is conducted in an open flask; the operation may be accelerated by passing a current of air through the apparatus. The authors have found that for a quantity of arsenic, not exceeding 0·2 gram, it is necessary to continue the boiling until about 500 c.c. water have distilled.

In this way arsenic may be separated from all other metals, and identified or estimated by the usual method, in the filtrate from the insoluble oxides.

C. F. C.

Determination of Cuprous Oxide in Copper. By W. HAMPE (*Zeitschr. Anal. Chem.*, 1878, 127—134).—Attention is called to Rammelsberg's paper (*Ber.*, x, 16) in which he states that the method of determining cuprous oxide in copper by silver nitrate is uncertain, and recommends ignition in hydrogen. The author refers to a notice in the *Zeitschr. für das Berg. und Hüttenwesen*, xxi, 218, in which the process is fully described, and in which it is shown that the reaction takes place as follows:—

$$3Cu_2O + 6AgNO_3 + xH_2O = 2Cu_2H_3NO_6 + 2CuN_2O_6 + 6Ag + (x - 3)H_2O,$$

and not as Rammelsberg considers it to be, viz.,

$$7Cu_2O + 14AgNO_3 = 14Ag + 4CuN_2O_6 + Cu_{10}N_6O_{25}.$$

E. W. P.

Estimation of Ammonia in Vegetable Products. By E. SCHULZE (*Zeitschr. Anal. Chem.*, 1878, 171—173).—The author proposes for the above estimation a combination of the methods of Sachsse and Schlösing, consisting of the following operations:—1. Determination of the nitrogen evolved by treatment with sodium hypobro-

mite both before and after boiling with concentrated hydrochloric acid, from the difference between which, the quantity of asparagin may be calculated. 2. Determination of the ammonia present after boiling with hydrochloric acid, and subtracting from this the quantity due to the re-solution of asparagin so as to obtain the quantity of ammonia originally present: for the latter it is recommended to *distil* with milk of lime. The author also recommends the removal of albuminous bodies, by precipitation with lead acetate, previously to the ammonia determinations.
C. F. C.

Paraffins in Commercial "Water-Gas." By H. MORTON and W. E. GEYER (*Chem. News*, xxxvii, 187).—Some experiments made by the authors with a "water-gas" (*i.e.*, a gas made by mingling the products of the reaction of steam and carbon, with oil-gas or like products of the decomposition of petroleum or naphtha) led to the conclusion that this material contained some members of the paraffin series, richer in carbon than marsh-gas itself. Such paraffins would, of course, play the part in such a gaseous mixture of practical illuminants, but not being absorbable by Nordhausen acid, would not be determined with the "illuminants" technically so called, in the usual process of gas analysis, and would be left to influence the results of those subsequent steps of the process which contemplate only the presence of free hydrogen and marsh-gas. In looking about for suggestions as to the proper treatment of such a mixture in order to analyse it, the question presented itself, can such a mixture be determined by any of the usual eudiometric methods? It is stated by Sutton and Bunsen, that a mixture of hydrogen and ethane may give exactly the same results as an equal volume of marsh-gas. Does this suggestion extend to any mixture of members of the marsh-gas series? Can even free hydrogen, as Fouqué supposes, be determined in presence of such a mixture?

To facilitate this discussion, the authors in the first place present a table of the volumes of carbonic acid formed, of contraction produced, of oxygen consumed, and of water vapour developed by the explosion in the usual manner of several members of the marsh-gas or paraffin series. Hydrogen is included in this table as the first of the series, for reasons which will presently appear:—

	H.	CH_4.	C_2H_6.	C_3H_8.	C_4H_{10}.	C_5H_{12}.
CO_2 formed....	0	1	2	3	4	5
Contraction....	$\frac{3}{2}$	2	$\frac{5}{2}$	3	$\frac{7}{2}$	4
O consumed....	$\frac{1}{2}$	2	$\frac{7}{2}$	5	$\frac{13}{2}$	8
H_2O formed....	1	2	3	4	5	6

In this table the

CO_2 formed increases regularly by 1 from 0 upwards.
Contraction ,, ,, $\frac{1}{2}$,, $\frac{3}{2}$,,
O consumed ,, ,, $\frac{3}{2}$,, $\frac{1}{2}$,,
Water formed ,, ,, 1 ,, 1 ,,

The CO_2 formed by 1 volume of hydrogen, the first member of this series, is $0 = 1 - 1$; by the second member it is $1 = 2 - 1$; by the third it is $2 = 3 - 1$. By any other member represented by n, it will be $n - 1$. The contraction produced by the various members will likewise be as follows:—

1st member, $\frac{3}{2} = \frac{3 + 1 - 1}{2}$. 2nd member, $2 = \frac{3 + 2 - 1}{2}$.

3rd member, $\frac{5}{2} = \frac{3 + 3 - 1}{2}$. nth member, $\frac{3 + n - 1}{2}$.

The oxygen consumed will be for the

1st member, $\frac{1 + 3 (1 - 1)}{2}$. 2nd member, $\frac{1 + 3 (2 - 1)}{2}$.

3rd member, $\frac{1 + 3 (3 - 1)}{2}$. nth member, $\frac{1 + 3 (n - 1)}{2}$.

The water formed will be, for the

1st member, 1. 2nd member, 2. 3rd member, 3. nth member, n.

By expressing by x, y, z, &c., the respective volumes of any number of such constituents, C_nH_{2n+2}, in a mixture of gases and vapours in which they occur, and indicating by V the total volume of the mixture; by C, the volume of carbonic acid formed; and by A, the contraction after explosion; by O, the oxygen consumed; and by W, the water vapour formed, the author shows that in the case of any one of these gases, or in the case of any mixture of any number of them, the following relations will hold:—

$$V = \frac{2A - C}{3} = 2O - 3C = W - C = \frac{3W - 2O}{2} = \frac{2A - W}{2}.$$

As a preliminary method for obtaining an approximate determination, the authors absorbed the substances under investigation in absolute alcohol; in place, however, of allowing for the added tension of the alcohol vapour, it was removed by absorption with Nordhausen acid. Allowance for the solution of hydrogen, marsh-gas, and carbonic oxide in the alcohol employed was also made. From the results obtained it appears evident that members of the paraffin series, pretty high in the scale, are present in water-gas, and that their average composition is probably about that of propane.

Water-gas made by the Municipal Co. of New York, working under the Tessié du Motay patents, and a variety made at Harrisburg, Pa., under the Lowe patent, gave the following results by the two methods of treatment.

	CO_2.	O.	Olefines.	CO.	CH_4.
Usual method	0·327	0·561	16·323	27·337	25·985
With alcohol		18·050		26·790	21·646
Usual method	3·403	0·340	11·782	27·216	21·740
With alcohol	3·402	trace	12·828	25·233	21·699

	H.	N.	Paraffins.
Usual method	24·889	4·572	—
With alcohol......	27·897	4·243	0·702
Usual method	32·567	2·945	not estimated
With alcohol......	34·548	1·408	0·869

D. B.

Estimation of Nitrogen in Nitroglycerin in Dynamite. By E. Ador and A. Sauer (*Zeitschr. Anal. Chem.*, 1878, 153—155).—The authors find that the equation of decomposition of nitroglycerin by potash,

$$C_3H_5.(O.NO_2)_3 + 3KOH = 3KNO_3 + C_3H_5(OH)_3,$$

is by no means realised in practice, ammonia being simultaneously formed in some quantity.

They also find that Schlösing's method for the estimation of nitrogen in nitroglycerin is uncertain, and that accuracy is possible only with Dumas' method of combustion with copper oxide. C. F. C.

Butter Analysis (Hehner's Method). By R. Sachsse (*Zeitschr. Anal. Chem.*, 1878, 151—153).—The author finds that the above method is applicable to extremely rancid butters, *i.e.*, that the loss of volatile fatty acids sustained by the latter is not sufficiently great to affect the percentage of non-volatile acids. C. F. C.

Butter Analysis. By W. Heintz (*Zeitschr. Anal. Chem.*, 1878, 160—166).—The author finds that in Hehner's method for the estimation of the soluble fatty acids in butter, it is unnecessary to filter previously to titration, the insoluble fatty acids being incapable of combination with the cold dilute alkali employed. This method is uncertain in presence of those acids, such as lauric, which are difficultly soluble in cold water. It is also subject to another source of error in the variation of the atomic weights of the soluble acids, the true weight of which cannot, therefore, be calculated from the amount of alkali neutralised. C. F. C.

Estimation of Glucose. By W. D. Gratama (*Zeitschr. Anal. Chem.*, 1878, 155—159).—This paper contains the results of a series of experiments undertaken with the view to ascertain the trustworthiness of the method proposed by Mulder for the estimation of glucose, which differs from Fehling's by involving the gravimetric estimation (as CuO) of the reduced copper oxide. With pure glucose and a given copper solution, constant results are obtained; but the author finds that the reduction equivalent of the latter, although constant for any given solution, varies in different solutions prepared after the same method.

His experiments also show that this method cannot be trusted for the estimation of glucose in presence of cane sugar.

These results render the trustworthiness of the volumetric method also questionable. C. F. C.

A New Copper Solution for the Estimation of Glucose. By H. Pellet (*Compt. rend.*, lxxxvi, 604—605).—The solution has the following composition:—

Copper sulphate, crystallised (pure)	68·7	grams.
Rochelle salt	200·0	,,
Sodium carbonate, dry (pure)..........	100·0	,,
Ammonium chloride	6·87	,,

The above salts are dissolved, by heating in a water bath, in 5—600 c.c. of distilled water, cooled, and made up to 1 litre; filtered, if necessary. The ammonium chloride acts as a preservative. The amount of glucose to which this solution is equivalent varies with the quantity of water present. The author therefore titrates with a standard solution of glucose, and when determining the amount of sugar present in a solution, employs as nearly as possible the same volume of water. For further details, the original paper must be referred to.

R. C. W.

Phloroglucin as a Test for Woody Fibre. By Wiesner (*Dingl. polyt. J.*, ccxxvii, 397).—Phloroglucin, a substance frequently occurring in the vegetable kingdom, will detect the smallest trace of woody fibre in the tissues of plants, in hemp, flax, and paper, by giving an intense violet to red coloration when these substances are moistened with a half per cent. solution of phloroglucin, and then with hydrochloric acid.

It is more delicate for this purpose than aniline sulphate.

A. J. C.

Separation of Cholesterin. By E. Schulze (*Zeitschr. Anal. Chem.*, 1878, 173—174).—In order to separate cholesterin from impurities which may accompany it in the ethereal solution in the ordinary method employed for its extraction, the author converts it into the cholesteryl-benzoic ether, by heating it for some time with benzoic acid or anhydride in sealed tubes. This compound is almost insoluble in boiling alcohol, by which therefore it can be freed from almost all impurities. It may then be crystallised from ether, and the well-formed shining plates converted into cholesterin by saponification with alcoholic potash.

C. F. C.

Tannin Estimation. By F. Kathreiner (*Dingl. polyt. J.*, ccxxvii, 481—490).—The author gives full details of an examination of Carpene's (Barbieri's) method. The results obtained varied with the amount of reagents employed, the rate of evaporation, and other details of manipulation. He is not prepared to recommend the method for adoption.

J. T.

Morphine Determinations. By J. Lynn (*Chem. Centr.*, 1878, 158; *Amer. J. Pharm.* [4], 6, 358).—The author examined by four methods as many samples of opium obtained from well-known firms. The opium was dried at 100° C. until it ceased to lose weight, and gave the following percentage amounts of morphine:—

	1.	2.	3.	4.
Proctor and Sharples' method ..	11·22	13·62	9·14	12·69
Mohr's method	11·40	13·48	9·30	12·77
Hager and Jacobsen's method ..	11·68	13·86	9·46	12·98
Dragendorff and Mayer's method.	12·33	14·00	10·40	13·06

Of the three gravimetric methods, that by Sharples gives the purest and best crystallised morphine, which is almost colourless, and can be easily collected. The method, however, requires more time than the others. Hager's is simple and quick, and can be completed in from four to six hours; the product is almost as pure as Mohr's. In both methods the crystals are incomplete and coloured. The morphine crystallises slowly and incompletely in the gravimetric methods. The volumetric method is preferable; it shows that appreciable quantities of opium are left in the mother-liquor. J. T.

Detection of Organic Poisons. By E. HEINTZ (*Zeitschr. Anal. Chem.*, 1878, 166—171).—The author recommends the addition of white bole (which has been purified by boiling with hydrochloric acid and subsequent washing) to solutions from which it is desired to isolate the alkaloïds. After evaporation, which is hereby accelerated, the dry residue is pulverised and exhausted with chloroform, or other solvent or solvents. The advantage of this method appears to be the removal by adhesive action of fatty, resinous, and other impurities without treatment with ether, which, in addition to its inconvenience, is liable to remove certain bodies which it is desired to retain, either by direct solution, or by taking up water holding them in solution.

The paper also contains the results of a number of experiments undertaken by way of verification and comparison. C. F. C.

Technical Chemistry.

Chrysoïdin, an Antiphotogenic Colour. By C. BARDY (*Chem. Centr.*, 109).—Chrysoïdin possesses the property of completely absorbing the chemically-active rays of light. The author proposes, as a substitute for the yellow glass, in a photographer's "dark room," to varnish the window-panes with a mixture consisting of 2½ grams of chrysoïdin, dissolved in 125 grams of warm water, 20 grams of gelatin, 3 of glycerin, and 40 grams of a 20 per cent. alum solution. Paper can be rendered impervious to actinic rays by immersion in a solution of 3 grams of chrysoïdin in 100 c.c. of alcohol and 50 c.c. of water. W. C. W.

Photographic Printing in Natural Colours. By KAISER (*Chem. Centr.*, 1878, 160).—J. Albert, of Munich, has succeeded in placing this process on a scientific basis. He has made known the principle of his method, but keeps secret the technical details. By decomposition, the elementary colours of an object are obtained in the relative strengths in which they occur in the original colour. These optical decomposition-products act on sensitised plates, with an intensity varying with their strengths. Thus, a pure green object will give a plate on which only yellow rays have acted, and another on which only blue have acted: from these plates two printing plates are prepared, one to print yellow, and the other to print blue. In this way the natural green of the object is reproduced. Only three colours are required to reproduce the various natural colours by this method, viz., a pure yellow, a pure blue, and a pure red. J. T.

Action of the Glover Tower. By F. Hurter (*Dingl. polyt. J.*, ccxxvii, 465—473).—Vorster (*Dingl.*, ccxiii, 411—506) maintained that the Glover tower acted as concentrator mainly, but as it acted objectionably as denitrating agent, so that a great part of the oxygen compounds of nitrogen become reduced to nitrogen. G. Lunge (*Dingl.*, ccxv, 56, ccxvi, 179) combatted the views of Vorster, in consequence of which, the latter (*Dingl.*, ccxv, 558) admitted that he had gone too far in asserting that in some circumstances 60 per cent. of the nitrogen compounds might be decomposed, but maintained that Lunge's calculations merely served to modify this view. The author had repeated Vorster's experiments before a second paper by Lunge (*Dingl.*, ccxxxv, 474—570, ccxxvi, 648) appeared, and he has obtained further results bearing on the point in question. His conclusions agree with those of Vorster.

The firm of Gaskell, Deacon, and Co. worked nearly two years with Glover towers without Gay-Lussac towers. Results of the working of the plant at this time show that by the application of the towers rather less than more nitre was used, but the saving is not sufficient to militate against Vorster's view.

Detailed experiments show that when NO_2 is absorbed by H_2SO_4, a mixture of NO_2 and N_2O_3 is always found in the acid.

In the works above cited, the nitrated acid was examined twice daily for a long time. The proportion of N_2O_3 to N_2O_4 by molecules was found to vary from 1 : 0·48 to 1 : 3·48.

The writer concludes that the nitrated acid (nitrose) of the works, as well as that of the laboratory, contains a variable mixture of N_2O_3 and NO_2, and that the latter is absent only when reducing agents have entirely converted it into N_2O_3, as when much sulphurous acid escapes at the Gay-Lussac towers. J. T.

Composition of Vitriol from Denitrating and Absorbing Towers. By G. E. Davis (*Chem. News*, xxxvii, 125—126).—From experiments made by the author, it appears that the arsenic in ordinary nitro-sulphuric acid from the absorbing towers is present in the state of arsenic acid As_2O_5, but after the elimination of the oxides of nitrogen, potassium permanganate shows the presence of 2 grams per litre, if the oxidant be calculated to nitrogen trioxide. From this it would appear that ordinary nitro-sulphuric acid contains substances other than nitrogen and arsenic compounds, which reduce permanganate potassium, probably ferrous sulphate and organic matter. Again the nitrogen exists in the acid as a mixture of nitrogen trioxide and peroxide. The various substances in grams per litre are:—

Arsenic acid (As_2O_5)	7·61
Nitrogen tetroxide (N_2O_4)	2·97
Nitrogen trioxide (N_2O_3)	7·68

In the case, however, of the acid running from the denitrating towers, the arsenic is contained in it in both states of oxidation, and it also contains small quantities of sulphur dioxide and nitric oxide, N_2O_2. The results obtained in grams per litre are:—

Arsenious acid (As_2O_3)	6·26
Arsenic acid (As_2O_5)	1·98
Sulphur dioxide (SO_2)	0·12
Nitric oxide (N_2O_2)...............	0·04

This was the acid which, after passing down the absorbing towers, gave the previous results. L. T. O'S.

Nitric Acid in the Vitriol Manufacture. By G. E. Davis (*Chem. News*, xxxvii, 155—158).—This paperdescribes some experiments which the author undertook, with a view of explaining the loss of nitre in the vitriol manufacture. Various vitriol exits were subjected to a complete examination, the following method being used:—A weighed quantity of pure caustic soda was placed in two aspiration bottles, with 20 c.c. of the strongest and purest hydrogen peroxide that could be obtained: one cubic foot of the escaping gases was drawn through the bottles. (1.) The acidimetric power was then taken, and the result calculated, per cubic foot to grains of sodium carbonate, neutralised by total acids. (2.) The sulphuric acid was precipitated and weighed as barium sulphate, and calculated to grains of sodium carbonate, which that amount of sulphuric acid would neutralise. The speed of draught in each case was taken with a tube anemometer, and the readings compared with the theoretical head of air calculated from the readings of two columns of ether in a U-tube; one end inserted into the flue, the other open to the air. The nitrogen trioxide in the vitriol was determined by the mercury method. The following exits were examined:

A. Six chambers, all in one series, exit from last chamber going direct to chimney; escape tests taken during one week, when exit was sulphurous. Working badly.

B. From same works, when working well.

C. Nine chambers worked in three threes. The three exits collected in one stream tower, packed with coke. Inlet to tower, straw colour. Exit from tower to chimney, colourless. Working well.

D. Brimstone acid works. Four chambers worked in one series. Exit from last chamber going direct to chimney. Working well.

E. Eighty-four tons Mason's pyrites burnt per week. Two Glover towers, one Gay-Lussac. Six chambers in one set.

F. Fifty tons Rio Tinto ore burnt per week. One concentrating column in one set.

G. Eighty tons Rio Tinto ore per week. Two concentrating columns, one absorbing column. Eight chambers working in one series.

The results may be tabulated as follows:—

	A.	B.	C.	D.	E.	F.	G.
Percentage of nitre used	3·4	4·7	—	—	—	—	—
Exit contains N_2O_3 in grains	1·8	1·8	1·07	1·5	0·35	—	—
				Exit flue.	Exit flue.	Exit flue.	Exit flue.
Area of exit pipe from chambers in sq. ft.	1·227	2·6	0·834	1·0	4·0	4·17	5·0
Speed of draught per second in feet	7·4	—	12·0	6·4	8·5	12·0	16·0
Cubic feet passing per week	—	—	—	3,870,720	20,563,200	30,240,000	48,384,000
Sodium nitrate per week in cwts. equal	34·5	50	28	—	21	32	42
At 95 p. c. to N_2O_3 in cwts.	14·6	21·2	11·87	—	8·925	13·6	17·8
N_2O_3 escaping per week in cwts.	12·6	19·4	8·24	7·4	—	—	—
O. V. running per week in tons at 123° T.	50	90	45	40	140	100	120
O. V. contains p. c. of N_2O_3 equal to	0·126	0·042	0·3	0·04	—	0·05	—
N_2O_3 per week in cwts.	1·26	0·756	2·7	0·32	—	1·0	—
O. V. contains p. c. of As_2O_3 equal to	—	—	—	—	3·5	0·07	0·4
As_2O_3 per week in cwts.	—	—	—	—	9·8	15·4	9·6
N_2O_3 reduced by As_2O_3 in cwts.	—	—	—	—	9·18	11·82	7·3
From these figures we obtain—							
N_2O_3 lost by exit from chambers in cwts.	12·6	19·4	8·24	7·40	—	—	—
„ in chamber acid „	1·26	0·756	2·70	0·32	—	1·00	—
„ by formation of nitric oxide „	—	—	—	—	7·52	—	—
„ by formation of As_2O_5 „	—	—	—	—	—	11·82	—
„ by As_2O_5 „	—	—	—	—	—	—	7·3
N_2O_3 unaccounted for „	0·74	1·044	0·93	0·78	—	—	3·62
„ lost by imperfect absorption „	—	—	—	—	1·660	—	6·88
Total N_2O_3 used	14·60	21·200	11·87	8·50	9·180	13·60	17·80

From the above it is seen that where towers are not used (A, B, C, D), the losses due to the escape of nitrous compounds from the chamber exit are, A, 86·3 per cent.; B, 91·5; C, 69·4; and D, 87·0 of all the nitrate used, and the percentages unaccounted for are, A, 5·0 per cent.; B, 4·9; C, 7·8; and D, 9·1, upon the total nitrate used. When towers are used, the results are very variable; and as the loss in E, F, and G seems due to arsenic, the author constructed the following table, which shows in column (1) the number of cubic feet of air passing the exit, per ton of O. V. at 123° T. per week; in (2) the percentage of nitrate rendered useless by arsenic; in (3) the percentage run away in chamber acid; and in (4) the lowest percentage of sodium nitrate upon the pyrites burnt, disregarding all losses but those in column (2):—

	1.	2.	3.	4.
E.	126,933	81·9	traces	1·03
F.	302,400	87·6	7·3	2·80
G.	336,000	41·0	traces	1·13

In conclusion, it is mentioned that, judging from these results, it would be perfectly safe to use only 0·26 per cent. of nitre upon the pyrites burnt. The author is now working towers supplied with sulphuric acid free from arsenic, when he hopes to have an opportunity of testing the truth of his theories. D. B.

Cement Testing. By C. Heintzel (*Dingl. polyt. J.*, ccxxvii, 508).—On working up cement with water, the finest particles become hydrated, and give a solid cement before the coarser particles become saturated. The greatest volume-change takes place when the cement is kept under water, as some contraction results on hardening in air. Bauschinger has made some experiments on the volume-change of various mixtures of sand and cement. The following table gives his results:—

Increase or diminution in side of a cube, originally 120 *mm. long, for the following admixtures of Cement and Sand, and on hardening in air and water.*

Cement : Sand.	1 : 0.		1 : 3.		1 : 5.	
Hardened in....	Air.	Water.	Air.	Water.	Air.	Water.
	Diminution.	Increase.	Diminution.	Increase.	Diminution.	Increase.
After 2 days ..	0·011	0·007	0·007	—	0·009	0·009
„ 4 „ ..	0·027	0·011	0·013	0·005	0·025	0·025
„ 1 week ..	0·053	0·011	0·040	—	0·051	0·051
„ 2 weeks..	0·075	0·020	0·062	0·002	0·082	0·052
„ 8 „ ..	0·115	0·015	0·109	0·002	0·126	0·125
„ 16 „ ..	0·164	0·025	0·144	0·009	0·166	0·166

Heintzel concludes that a good cement should not fracture a test-tube during the first four weeks, but that the glass test leads to erroneous results. J. T.

Preparation of Sulphate of Alumina for Paper-making. By RADEMACHER (*Dingl. polyt. J.*, ccxxvii, 382).—This paper is a criticism upon a commercial sulphate of alumina which the author considers has been prepared from bauxite, and is, therefore, quite unsuitable to be employed in the manufacture of paper. A. J. C.

The Glaze of Red Roman Pottery. By F. KELLER (*Dingl. polyt. J.*, ccxxvii, 509).—In the district of Rheinzabern in the Pfalz, 70 Roman pottery furnaces and 36 brick-kilns have been discovered. With the excellent clay from this locality, F. Keller has obtained the thin, shining, transparent glaze of the antique ware. J. T.

Production of Zinc in the Blast-furnace by a Continuous Process. By W. KÖHLER (*Dingl. polyt. J.*, ccxxvii, 384—390).—The methods at present employed for the production of metallic zinc are extremely costly in fuel and in metal. In addition to the loss of metal by oxidation and volatilisation, there is the difficulty of obtaining a perfect condensation of the zinc vapour, which on that account is deposited in a finely divided condition instead of in a fluid form. In this paper the author discusses Clerc's method for the production of zinc by a continuous process in the blast-furnace (*Dingl. polyt. J.*, ccxxiv, 179). It is considered that it will be possible thereby to obtain the metal by a continuous process without risk of oxidation, and by maintaining a constant temperature for the condensation of the zinc vapour, it will be deposited in a fluid state.

An apparent difficulty is to prevent the re-oxidation of the metal in the furnace. This is said to be accomplished by employing roasted ores free from foreign oxides, and a thick stratum of coal; then blasting sufficient hot air to give a zone in the furnace of such a temperature and dimension, that therein all the CO_2 is reduced to CO before the temperature has fallen below 1000°, the reducing temperature of zinc oxide. A. J. C.

A Chromium Blue. By G. BONG (*Bull. Soc. Chim.* [2], lxxxix, 201).—A blue, capable of resisting a high temperature in the presence of materials used in the manufacture of porcelain, may be obtained by calcining strongly a mixture of 15 parts of boric acid, 15 of alumina, 20 of carbonate of manganese, and 2 of barium chromate.

L. T. O'S.

Conversion of Chromium Oxide into Chromic Acid in the Wet Way. By R. WAGNER (*Dingl. polyt. J.*, ccxxvii, 368).—The chromium oxide which is contained in the residues from the oxidation of anthracene by potassium chromate, is recommended to be reoxidised by heating these residues with a mixture of soda lye and potassium ferricyanide. In a very short time the chromium oxide is completely converted into the yellow chromate. This method has the advantage of forming potassium ferrocyanide as a bye-product.

Potassium permanganate and chloric acid, although quite as effective as potassium ferricyanide, are too costly for this purpose, and bleaching powder has the disadvantage of producing chlorine compounds in the liquid.

According to Waage and Kämmerer the re-oxidation of the chromium residues can also be effected by heating them with soda-lye and adding bromine in small quantities until the solution becomes clear and yellow. A. J. C.

Preparation of Iron and Steel Direct from the Ore. By W. Siemens (*Chem. Centr.*, 1875, 105).—At the autumn meeting of the Iron and Steel Institute, held at Newcastle, the author gave some further remarks regarding the production of iron and steel by the direct process. Three rotatory furnaces were erected at the Towcester Works. About 30 cwt. of ore mixed with 9 cwt. of small coal having been charged, the furnace is rotated for 2½ hours; the slag is then tapped, and the speed of rotation increased to ball up the iron. The balls formed contain about 70 per cent. of iron and 30 per cent. of cinder, but it is found that the particles of iron are pure metal, although the slag may contain 6 per cent. or more of phosphoric acid and from 1 to 3 per cent. of sulphur. The bulk of the cinder is removed by shingling, but sufficient remains to impart to the fracture a dark appearance without any sign of crystalline texture. The metal shows in being worked what may be termed "slag-shortness." By repiling and reheating, crystalline iron of great purity and toughness is produced. Mr. Samuel Lloyd suggested treatment in the charcoal refinery hearth instead of the repiling.

The following table shows the composition of some of the irons produced:—

	1.	2.	3.	4.	5.	6.	7.
Fe	98·30	98·73	99·45	98·97	98·909	—	99·907
Si......	·745	·243	·643	·565	·582	—	·640
C	—	—	—	·235	·225	·15	·100
P	·08	·032	·03	·019	·02	—	·128
S	·065	·071	trace	·085	·106	·09	·035
Mn.....	·144	·101	trace	·126	·158	—	trace

	8.	9.	10.	11.	12.	13.
Fe	99·128	98·728	—	99·711	99·278	99·199
Si	·717	·932	—	·065	·316	·4
C......	trace	trace	—	·12	·12	·15
P......	·125	trace	·024—·172	·077	·073	·05
S......	·03	trace	—	·27	trace	trace
Mn	·228	·34	—	trace	·213	·201

	14.	15.	16.	17.	18.
Fe......	—	—	—	—	—
Si	·316	·155	·23	·026	·027
C	trace	trace	trace	·1	·1
P	·019	·046	·083	·09	·093
S	trace	trace	·06	·021	—
Mn	trace	trace	trace	trace	—

1. Hammered iron, 9th August, 1875.

2. Iron from Canadian ore, 18th August, 1875.
3. ,, Towcester ore, 25th ,,
4. ,, ,, well rolled at Darlaston, 15th September, 1875.
5. ,, ,, badly rolled at Darlaston, 15th September, 1875.
6. ,, ,, badly hammered, containing slag.
7. Chatterley, 13th October, 1875.
8. Towcester iron, rolled at Darlaston. ·717 Si corresponds to 1·54 per cent. of slag.
9. Iron from Indian ores, November, 1875, ·932 Si corresponds to 2 per cent. slag.
10. P in Towcester iron.
11. Homogeneous iron, from Towcester iron, produced at Darlaston, June, 1876.
12. Towcester iron, rolled at Darlaston, August, 1876.
13. ,, ,, Northampton, August, 1876.
14. Towcester iron-bloom, containing 3·17 per cent. slag.
15. Iron, fractured bloom 26 C., crystalline texture, slag 1·58 per cent.
16. Iron, fractured bloom 26 C., texture fibrous and dull, slag 2·61 per cent.

17 and 18. Iron re-melted in the refinery.

J. T.

The Bessemer Process. By F. C. G. Müller (*Deut. Chem. Ges. Ber.*, xi, 536—556).—The process was investigated at the iron and steel works, Osnabrück.

Samples were taken at intervals from charges 22568 and 23006, and analysed with the following results:—

I. *Charge* 22568.

	Charge.	After 5 min.	After 10 min.	After 18 min.	40 secs. after addition of Spiegel.
C	3·46	2·71	1·417	0·092	0·105 0·133
βC ..	3·18	—	—	—	—
Si....	1·94 1·92	1·07	0·79	0·532	0·346
Mn ..	2·99	1·92	1·36	0·538	0·621

II. *Charge* 23006.

	Charge.	After 5 min.	After 9 min.	After 14 min.	After 16½ min.	15 secs. after addition of Spiegel.
C ..	3·39	2·69	1·591	0·419	0·046	0·142
βC..	3·10	0·438	0·251	0·223	0·019	0·104
Si ..	1·73	1·02	0·927	0·943 0·945	0·514	0·445
Mn .	2·63	2·29	1·84	1·44	0·914	0·716

The first charge proceeded normally, whilst the second one was exceptionally violent, although both consisted of $\frac{2}{3}$ Georg-Marien iron and $\frac{1}{3}$ English hæmatite. In the first five minutes the second charge produced a large quantity of half-fused cinder. After the addition of 5 per cent. of spiegeleisen at the end of the blow the previously half-fused cinder became quite fluid. After 9 minutes and until 14 minutes, the air-pressure was reduced from 23 lbs. to 13 lbs.

A graphic representation of the Analysis II shows that the silicon burns quickly during the first five minutes, much more slowly up to nine minutes, and then not at all up to 14 minutes, so that the percentage composition increases a little. No. I is similar so far as it goes. The two carbon curves are almost identical. The two manganese curves are almost straight lines, that in I being steepest, apparently in correlation with the steeper silicon curve.

In charges which explode violently, the manganese burns more slowly, and the silicon ceases to burn sooner than in less violent charges. The former yield steels with high percentage of silicon and manganese, thus:—

	1.	2.
C............	0·222	0·111
Si............	0·566	0·353
Mn..........	0·908	0·714

To test this view, two different samples of metal which had been thrown out of the converter were analysed:—

	3.	4.
C	0·53	0·96
Si............	0·70	0·84
Mn	2·17	2·45

The pig-iron had from 3·5 to 5 per cent. of manganese. The pig-metal and steel of a quiet blow, in which nothing was expelled, gave

	5.	6.
C	3·36	0·205
βC............	3·02	—
Si............	1·81	0·283
Mn	5·04	0·466

Bessemer metal containing 1·5 per cent. of silicon, but at the highest only 0·2 per cent. of carbon, is highly regarded both in France and England (*Jour. Iron and Steel Inst.*, 1877, i, 40—85); according to Gautier, good steel has been obtained containing 7·0 per cent. (!) silicon at Terrenoire (*ibid.*, 44). Formerly only silicon-free Bessemer metal was produced, as is shown by the existence of the still prevalant idea of the injurious influence of silicon.

The removal of carbon, silicon, and manganese during the process is generally considered as due to a process of direct burning. Theoretical considerations show this to be very improbable. The only element which exists in approximately the same quantity, and therefore burns uniformly during the 5—14 minutes' time when the temperature is constant, is the iron. The oxide formed dissolves, and the oxygen passes over to the elements in combination. The possibility of the Bessemer process rests on the property analytically proved by Bender (*Berg und Huttenwesen-Zeitung*, 1872, 261), that fused iron can dissolve a considerable amount of its own oxide. It is known that direct burning of the metalloids plays very little part in the puddling process, and the phenomena of eruption in the converter, and of boiling in the puddling furnace cannot be explained without introducing indirect burning.

The behaviour of the carbon, silicon, and manganese towards the dissolved oxide depends both on the quantity of these elements present and on the temperature. Analysis II shows that the initial temperature is not sufficient to ignite the carbon. Sometimes in so-called cold charges, even after 15 minutes, no carbon at all is burnt, although the βC always disappears after a few minutes. After the temperature has been raised by the burning of the silicon during the first three minutes, the carbon is rapidly attacked, and the violet carbonic oxide flame is the result. This action begins at a certain minimum temperature, and this critical point marks the end of the first period of the process. The burning of the silicon almost entirely ceases, in consequence of which the temperature remains nearly constant, for the burning of the whole of the carbon would not raise the temperature 50°. In absence of manganese, the temperature would fall, so that a little more silicon would be burnt. The manganese burnt is blown out as Mn_3O_4; it does not pass into the cinder, as SiO_2 is not formed at the same time, and the half-fused cinder formed during the first period does not become more liquid during the second one. The third period commences when the carbon has reached a minimum of 0·02 per cent.; the silicon burns more actively again, the disturbance in the converter diminishes, and the flame becomes smaller. A charge which, through a defect in the converter, had to be run out at the end of the second period, gave by analysis—

C	0·043
Si	0·049
Mn	0·062.

Here the carbon is almost the same in amount as in Analysis II.

The third period is accompanied by a considerable excess of oxygen in the bath, by which the remainder of the silicon is burnt. The SiO_2 formed takes up FeO, and the well-known brown cinder is produced, whilst previously the cinder was mainly an acid manganese silicate. The excess of oxygen is also indicated by the strong combustion which follows the addition of spiegel.

Silicon burns out quickly after the addition of spiegel; this seems to result from the cooling of the bath; the two following experiments seem to support this view. Cold rail-ends were added to one of two successive charges, of the same initial composition, towards the end of the blow. The silicon was estimated in the resulting metal of both charges before any addition of spiegel.

	3 per cent. of rail ends added 2 minutes before end of blow.	Same charge without addition of rail ends.
A. Si.	0·364 per cent.	0·512 per cent.

This was repeated with the following result:—

	5 per cent. of rail ends added $4\frac{1}{2}$ minutes before end of blow.	Same charge without addition of rail ends.
B. Si..........	0·205 per cent.	0·450 per cent.

From this it is concluded that the affinity of silicon for oxygen is relatively lower at high temperatures. This agrees with blast-furnace practice and with laboratory results.

The less the amount of carbon in Bessemer pig, the less time will be required in the converter. An ideally perfect pig would contain nothing beyond 2 per cent. of silicon.

The cinder produced at Osnabrück consists mainly of manganese silicate, with not more than 7 per cent. of iron oxide usually.

	I.	II.	III.
SiO_2...............	53·5	52·7	43·73
MnO..............	36·5	38·2	45·41
FeO	6·7	6·5	9·04
Al_2O_3..............	—	—	1·99
CaO	—	—	trace
			100·17

I and II are partial analyses of ordinary cinders; III is the analysis of a crystalline cinder which had been cooled very slowly. By ignition the finely powdered cinder is oxidised, and the increase in weight is sensibly proportional to the amount of iron protoxide present, a compound corresponding to $FeMnO_3$ appearing to be formed: this absorbed oxygen appears to be expelled again at a higher temperature.

J. T.

Malleable Iron Castings. By P. v. TUNNER (*Chem. Centr.*, 1878, 158—159).—For this purpose a proper quality of cast-iron is essential. A relatively pure iron, suitable for the production of good bar iron, or good steel, will give good malleable castings. The only other condition is that the iron should be sufficiently liquid, when hot, to fill the mould. A light grey charcoal iron, prepared from pure ores, is very suitable.

As decarbonising agent, finely-powdered red hæmatite or iron glance may be used, or, in place of these, roasted spathose ore, brown ironstone, or magnetic iron ore may be employed.

J. T.

Kaiser Oil. By M. BUCHNER (*Dingl. polyt. J.*, ccxxvii, 381).—This oil has been lately introduced into Austria for illuminating purposes. It is opalescent, nearly colourless, and has a slight petroleum odour. Sp. gr. ·7924 at 16·8°. The flashing point was 51°, the oil took fire at 62°. When distilled it gave 3 per cent. of distillate at 90—170°; 45 per cent. at 170—200°, and 43 per cent. at 200—300°, or a total distillate of 91 per cent. The residue solidified at 6°. The photometric intensity of kaiser oil is between 6 and 15 per cent. greater than petroleum oil, but it costs about 45 per cent. more.

A. J. C.

Use for a Constituent of Gas Lime. By T. DOUGLAS (*Chem. News.*, xxxvii, 126).—The author has obtained ferrocyanides from gas lime, which generally contains large quantities of thiocyanates. By mixing it with 5 per cent. of soda-ash, extracting with water, evaporating, and fusing the residue with soda-ash and iron filings, a product is obtained which yields ferrocyanides when boiled with water. This seems to offer a ready method for freeing gas lime from at least a portion of its sulphur, and therefore may prove to be of commercial value. L. T. O'S.

Analysis of Cane- and Beet-root Sugar Ash. By J. W. MACDONALD (*Chem. News*, xxxvii, 127).—The following are the results of analyses made of samples obtained by preserving the ashes of all cane and beet-root sugars analysed in a large sugar refinery during one year, and therefore, as far as the bases are concerned, may be taken as representing the average composition, but the volatile acids have been expelled by the sulphuric acid employed in the sugar analysis.

	Cane Ash.	Beet Ash.
Potash	28·79	34·19
Soda	0·87	11·12
Lime	8·83	3·60
Magnesia	2·73	0·16
Ferric oxide and alumina	6·90	0·28
Sulphuric anhydride	43·65	48·85
Sand and silica	8·29	1·78
	100·06	99·98

L. T. O'S.

Constant Ratio between the Ash and the Non-Sugar ingredients of Sugars. By F. STROHMER (*Chem. Centr.*, 1878, 168—174).—A controversial paper, calling in question Gawalovski's statement that he had succeeded in establishing the existence of a constant ratio between the ash and the non-sugar ingredients in the first products of the sugar refinery. The author's experiments show that no such constant ratio exists. M. M. P. M.

Comparative Analysis of Rhubarb. By DRAGENDORFF (*Pharm. J. Trans.* [3], viii, 826—829).—Five samples of rhubarb were analysed for comparison, namely:—

I. *Rheum Moscovicum*, imported in 1860 with the last consignment of the crown rhubarb.

II. *Rheum chinense*, delivered from the Crown Warehouse, St. Petersburgh, 1877.

III. *Rheum palmatum tanguticum.*

IV. *Rheum anglicum cultum* from Moscow.

V. Rhubarb cultivated in Siberia.

A detailed account of the analyses is given, the results of which will be seen in the following table.

	I.	II.	III.	IV.	V.
Moisture	9·52	11·25	10·35	11·09	8·69
Ash	8·27	6·32	24·05	3·20	10·38
Mucilage soluble in water	3·35	1·58	1·71	2·55	3·08
Arabic acid soluble in water not precipitated by alcohol	5·82	6·43	3·17	8·32	2·01
Metarabic acid	3·82	5·70	2·57	3·22	8·47
Pararabin	3·91	2·10	3·54	1·95	3·02
Starch	8·40	6·20	6·32	16·50	11·95
Cellulose	7·45	7·64	4·91	4·29	8·61
Sugar	5·55	4·29	3·94	4·40	3·66
Substance readily soluble in absolute alcohol, probably a carbohydrate	2·70	6·47	7·41	8·21	1·95
Cathartic acid	5·25	4·88	2·03	2·50	2·26
Malic acid, &c.	0·04	1·09	trace	0·17	1·24
Calcium oxalate	3·28	4·59	4·19	1·12	2·15
Chrysophanic acid soluble in petroleum spirit	—	trace	trace	trace	1·01
Chrysophan and tannin	17·13	14·17	8·22	4·83	7·84
Emodin, erythroretin, phæoretin, &c.	1·13	1·15	1·18	5·89	6·29
Dark brown crystalline resin, &c., soluble in alcohol and ether	1·00		2·59		
White crystalline resin soluble in ether, insoluble in alcohol	0·15	0·70	0·49	2·32	2·75
Fat	0·05	0·15	0·32	6·17	trace
Albuminoïd substances	4·37	4·39	4·33	3·17	3·92
Paracellulose, vasculose, pectose, lignin, &c.	18·81	10·90	8·68	16·10	10·72

The author considers the active constituents of rhubarb to be (1) cathartic acid, to which it owes its purgative properties, and (2) tannin and chrysophan, which render it so valuable as a tonic; it is therefore evident that Nos. I and II are superior for medicinal purposes.

L. T. O'S.

Preparation of Liquid Indigo-carmine. By v. JOCLÉT (*Chem. Centr.*, 1878, 157).—Pure finely-ground indigo is added gradually to five times its weight of pure sulphuric acid heated to 36—40° R. To this is then slowly added crystallised carbonate of soda to the amount of three times the quantity of indigo taken, the soda being first dissolved in ten parts of water. After being stirred at times for twelve hours and allowed to stand until carbonic anhydride ceases to be evolved, the liquid carmine is filtered off through a cotton-wool filter. The residue on the filter is pure indigo-purple.

J. T.

On the Water used in Dyeing Woollen Goods. By G. JARMAIN (*Dingl. polyt. J.*, ccxxvii, 196—199).—Organic matter, iron oxide, and calcium carbonate are the impurities which most affect the materials in the process of dyeing. The organic matter and iron oxide cause little spots to appear, and the latter also affects the shade and purity of colour. Calcium and magnesium carbonate precipitate an insoluble soap in the woollen materials, which is difficult to remove, and which interferes with the mordanting. This can be avoided by boiling the water with soap, and filtering or skimming off the insoluble lime and magnesian soap. Even after the stuffs have been dyed, however, the presence of lime carbonate in the water used for washing them affects the colour. Thus cochineal and logwood take a bluish shade when washed in such water. The water used should not have a greater hardness than 7° of Clark's scale, of which 2° are due to permanent hardness, which does not affect the dyeing.

A solution of logwood is a very sensitive reagent for testing waters. 1 part of logwood powder dissolved in 4 parts of distilled water is added to about 100 c.c. of the water to be tested. The presence of chlorides or sulphates of magnesium and calcium is indicated by a reddish-brown coloration. The presence of carbonates is detected by the wine-red colour, which has a tinge of blue. Iron causes an olive to blue-black coloration. Alkaline carbonates give a dark cherry-red. Water with free acid gives a clear yellow. S.

Red Colour Reaction of Wood. By A. KIELMEYER (*Dingl. polyt. J.*, ccxxvii, 584).—The violet-red coloration which Wiesner obtained by treating wood with phloroglucin and an acid led him to raise the question, whether this reaction could be used in practice for dyeing woody textures and cells, *e.g.*, jute. The author thinks that in order to answer this question satisfactorily various points must be investigated. Since an acid is required for the dyeing operation, it will be necessary to determine whether, after treatment with water, soap, or soda, and drying, the red colour is retained in the dyed material, and whether the colour is not altered by exposure to air or light. It may be interesting to mention that in 1872 Kielmeyer obtained a similar colour reaction with pine-wood. By boiling anthracene with three parts of nitric acid (sp. gr. 1·3298) and forty parts of strong alcohol a nitro-compound was obtained, which after reduction with zinc-dust gave an organic base, the acid solution of which dyed pine-wood with a characteristic blood-red colour. Cotton is dyed very badly. This reaction is a very satisfactory test for ascertaining the presence of woody matter in paper or other materials, the red coloration being more distinct than the yellow one obtained with anilin-salts. D. B.

Sizing Paper. By C. WURSTER (*Dingl. polyt. J.*, ccxxviii, 267—269).—This is a reply to a paper by A. Tedesco (*ibid.*, ccxxvi, 600), criticising a previous paper of the author's. The latter states that in a dilute solution of rosin soap containing free rosin, the latter separates as an emulsion, but does not collect together even on boiling. In a concentrated solution, however, the liquid becomes yellow at a certain temperature, and the free resin is rapidly deposited in a flocculent state. D'Arcet obtained well sized paper with 1 per cent. of rosin, the starch being 12 per cent.

The lead salt, obtained by precipitating with lead acetate an alcoholic solution of resin neutralised with ammonia, melts at 127°; the corresponding aluminium compound melts above 300°. The author asserts that the aluminium salt obtained by Tedesco was sulphate, and not a resinous salt. J. T.

Composition of Meat impregnated with Common Salt. By M. Rubner (*Zeitschr. f. Biologie*, xiii, 513—517).—The author has made an examination of meat preserved by Eckart's process, namely, impregnation under high pressure with a 25 per cent. solution of salt, and subsequent smoking. The outer portions of pieces prepared in this way were found to contain less water and more solid matter than the inner parts, but the percentage of salt was uniform throughout (= 10 per cent.).

To determine the effect of salting alone, 30 kilograms of fresh beef, in large pieces, were treated with a solution of 16·5 kilos. salt in 50 litres of water. After 24 hours the meat had increased in weight by 650 grams, or had absorbed 1,913 grams of salt and lost 1,263 grams of water. The salt solution contained no albumin and but little organic matter (·41 gram per 100 c.c.). The meat had given up about 11 per cent. of its phosphoric acid—less than one-fourth of the loss during the ordinary process of salting. In the latter process, indeed, pork has been found by Thiel to lose as much as 87 per cent. of its phosphoric acid.

Eckart also preserves meat by treating it for a quarter of an hour with a solution of 500 grams of salicylic acid in 100 litres of water. Meat prepared in this way keeps well, and is apparently unchanged in composition and flavour. Ch. B.

Preparation of Copal Varnish. The Composition of Copal and its alteration by Fusion. By H. Schwarz (*Dingl. polyt. J.*, ccxxvii, 374—381).—The best kinds of copal varnish are prepared by melting East Indian or East African copal, and dissolving the melted product in linseed oil varnish, and turpentine oil. After being melted, the copal becomes soluble in ether, chloroform, benzene, and carbon bisulphide, but these solvents give a varnish, which dries brittle. A brilliant varnish can be obtained by working up manganese borate, and minium with the linseed oil, and then gently heating to decompose the oil.

The author describes the apparatus employed to melt the copal, and the necessary precautions to follow in the melting operations. Galvanised iron melting pots have been employed with advantage instead of copper, which frequently gives a reddish sediment to the melted copal. A good copal varnish can be made by melting 1·5 kilograms of copal for 20 minutes with frequent stirring, then adding 3·5 kilograms of linseed-oil varnish, and 1·75 kilograms of French turpentine oil.

An almost colourless specimen of copal, dried over sulphuric acid, gave on analysis C = 78·72, H = 10·24, O = 11·09. The author doubts the possibility of isolating the resins in copal by the alcohol method of Unverdorben, who considered that he had thus separated five resins from African copal.

When copal is successively exhausted with cold dry ether, there remains undissolved a gelatinous swollen mass, which on that account the author terms "schwell-copal." Copal can be thus separated into two portions, one soluble and the other insoluble in ether.

Insoluble in Ether.—Copal contains 66 per cent. of "schwell-copal," hence the reason it is impossible to use crude copal for varnish making. "Schwell-copal" when once melted is rendered soluble in ether. Dried at 170° it gave C = 79·95, H = 10·87, O = 9·18.

Soluble in Ether.—The residue from ether remains liquid at 100°, owing to the presence of an ethereal oil, which may be expelled by heating at 130°. Dried at 130° it gave on analysis C = 78·25, H = 10·30, O = 11·70. It is called soluble copal.

Melted Copal or Pyrocopal.—Copal when sufficiently melted to be rendered soluble in the usual solvents, loses between 5 and 12 per cent. by weight. The evolved gases were analysed, and gave per cent. CO_2 = 35·6, CO = 32·20, H and CH_4 = 32·20. Pyrocopal is dissolved by ether, benzene, carbon bisulphide, and carbolic acid, but is most soluble in chloroform; it is also dissolved by hot linseed oil and turpentine oil. It contains C = 83·63, H = 10·36, O = 6·01.

When a chloroform solution of pyrocopal is poured into absolute alcohol, a fine yellowish mass is separated, which is quite insoluble in alcohol. It is called "pyroschwell-copal." Dried at 100° it gave C = 83·01, H = 10·52, O = 6·47. Pyro-soluble copal was obtained from the alcoholic solution, as a hard brownish resin. It contained C = 81·02, H = 10·37, O = 8·61.

In all cases, melting the copal causes an increase in the percentage of carbon, and a decrease in oxygen and hydrogen.

The author does not assert that the resins which are separated in this manner are absolutely definite compounds, but it is interesting to construct the formulæ on the above data:—

Crude Copal, $C_{19}H_{30}O_2$.	Pyrocopal, $C_{19}H_{28}O$.
"Schwell-copal," $C_{48}H_{76}O_4$.	Pyroschwell-copal, $C_{48}H_{74}O_3$.
Soluble copal, $C_{36}H_{56}O_4$.	Pyro-soluble copal, $C_{36}H_{54}O_3$.

When cautiously distilled, copal gives but little carbonaceous residue; no compounds or products of decomposition have been obtained.

A. J. C.

General and Physical Chemistry.

Researches on the Absorption of the Ultra-violet Rays by Various Substances. Note by J. J. Soret (*Compt. rend.*, lxxxvi, 708—711).—With a spectroscope having a fluorescent eye-piece, the phenomena of absorption for the ultra-violet rays can be observed with great facility. The author has employed such a spectroscope with quartz prisms and lenses, and with it has studied a large number of bodies which are colourless in the ordinary sense, but still intercept a part of the invisible rays. For the source of light induction sparks were used, and the parts of the spectrum specially studied were the cadmium lines to 26, the last three zinc lines 27—29, and the last three aluminum lines 30—32. He not only confirms Professor Stokes's result that quartz exercises a sensible absorption upon the aluminum line 32, but finds in addition that lines 27 to 30 are weakened; and by a sufficient thickness of Iceland spar are altogether stopped. Distilled water of 10 mm. thickness is less transparent than quartz, but for greater thicknesses it is more transparent: for 1·16 m. of water allowed the zinc line 28 to be distinguished, but it was stopped by a very much smaller thickness of quartz. It may therefore be considered as almost perfectly transparent.

In aqueous solutions, the absorption depends upon the strength of the solution, not upon the quantity of water.

Bases and acids carry their absorbing properties into salts.

Besides the iodides, nitrates, and alkaloïds, which have already been examined by Stokes and Müller, the author mentions that many other substances gave rise to absorption-bands in the ultra-violet, such as alkaline chromates and bichromates, potassium nitrate, sulphates of didymium and cæsium, potassium permanganate, and sulphurous acid in solution.

The author considers that quantitative determinations could be made for some of these bodies by spectrum analysis. J. H. P.

Ultra-violet Absorption Spectra of the Gadolinite Bases. By J. L. Soret (*Compt. rend.*, lxxxvi, 1062—1064).—On examining the absorption spectra of the bases in gadolinite by means of sunshine and a prism of Iceland spar, characteristic bands were observed in the ultra-violet rays, which the author considers are not due to yttrium, erbium or terbium, but to the new base discovered by Delafontaine (*Archives des Sciences physiques et naturelles*, 1878, 273).

W. C. W.

Transparency of Coloured Flames. By Gouy (*Compt. rend.*, lxxxvi, 878—880).—These researches have been made partly by the photometer already described (*ibid.*, lxxxiii, 269), and also by a method which the author describes in the present paper, and which permits of the measurement of very feeble radiations.

The coloured flames were produced by the combustion of a homogeneous mixture of illuminating gas and air holding some metallic salt in suspension. As the regulation of the flames constituted one of the chief difficulties of experimenting, a regulator for the gases was devised which entirely prevented any variations in the pressure of gas or air.

The flames are slightly reducing in their action, and the temperature is sensibly the maximum given by a mixture of air and gas.

The following is a short description of the method the author employs. The objective of the collimator of a spectroscope is half covered by a plain mirror, which receives the rays proceeding from a second collimator, so as to render them after reflection parallel to the axis of the first. Two superposed spectra are thus obtained in the same focal plane, these being received on a slit parallel to the rays, which serves instead of an eye-piece.

Each of the two flames to be compared sends its rays into one of the collimators, so that the eye placed at the slit sees through the prism one half of each of the two objects as a circle of which the halves are of the same colour, but differ in brightness. The same intensity may be given to them by two Nicol's prisms, with which the second collimator is provided; the angle between their principal sections as read from a graduated circle, enables the result of the experiment to be calculated.

Transparency of Flame for Rays it does not itself Emit.—The rays of a lamp provided with a regulator are received in the apparatus in such a manner as to compel them to traverse the coloured flame. These experiments are conducted in such a manner that the refraction produced by the flame cannot interfere. The author has employed very bright flames charged with Na, Li, Ca, and Sr, and in all cases the flames were found to be quite transparent; absorption, if it existed, being certainly less than $\frac{1}{50}$.

Transparency of the Flame for Rays emitted by itself.—To give precise significance to the results, the following measurements were made; a homogeneous layer of incandescent metallic vapour being given, on doubling its thickness, other conditions remaining constant, the brightness of one of the rays or bands, or of the continuous spectrum which it gives when multiplied by a factor k is found to be comprised between 2 and 1. This factor the author has measured by two methods: (1.) By placing behind a coloured flame a second flame identical with the first; (2) by placing a flame at the centre of a mirror whose reflecting power is known; these two methods gave concordant results. The author explains also what he means by the *intensity of a spectral line*. Placing in front of the flame an absorbing medium which only allows the rays constituting the line or band to be studied to pass, and comparing its intensity with that of a luminous surface of the same colour but invariable intensity, the result will be the intensity of the flame, or rather the brilliancy of the line compared with an arbitrary unit.

For continuous spectra of K, Na, Al, Mg in brilliant flames, k is found equal to 2, and they are consequently completely transparent. For the principal bands of Sr, Ca, and Ba, *k* is found to be comprised between 1·94 and 2. There is in this case therefore a little absorption.

J. M. T.

Variation of the Indices of Refraction in Mixtures of Isomorphous Salts. By H. Dufet (*Compt. rend.*, lxxxvi, 881—884).—It is known that isomorphous salts present certain analogous optical properties; thus in crystals belonging to the system, having two optical axes, the direction of the double refraction is generally the same, and the indices arranged according to their numerical order, correspond generally with the same crystallographic axes.

Researches on this subject have been made by Senarmont, who observed that in certain isomorphous crystals the double refraction varied with change of sign; he concluded therefore that there was no analogy between the crystalline form and the optical properties.

The author then alludes to the criticisms of MM. Haldor, Topsoë and Christiansen, published in the *Ann. Chim. Phys.*, 1874, who determined the values of the principal indices in a number of salts, and proved that there is an analogy, although in certain cases the difference between the indices is very great in proportion to that of the crystallographic parameters.

In place of studying simple isomorphous salts, the author has examined mixtures of such salts of known composition, especially sulphates of the magnesium group, and gives the results obtained with magnesium and nickel sulphates containing 7 molecules of water. These sulphates all crystallise in orthorhombic prisms of about 91°; the angle however for the nickel salt is 91·10°, for the magnesium 90·30. He finds that the bisection of the acute angle of the optic axis coincides with that of the acute angle of the prism; and it is easy by cleavage to obtain faces perfectly normal to this bisection, and to cut prisms having their refracting edge parallel to the edges of the crystal, giving the mean index by the deviation of the ordinary image.

The author has studied five of the mixtures of magnesium and nickel sulphates of which the composition has been determined. He finds that the index increases regularly as the proportion of nickel increases. He has also repeated for the simple sulphates the determinations of the principal indices, and has obtained numbers agreeing with those of Topsoë and Christiansen in the case of the magnesium salt, but the numbers for the nickel salt are slightly higher.

The following experimental law was found to obtain for mixtures of these salts. The differences between the indices of a mixture of two isomorphous salts and those of the component salts, are in the inverse proportion to the number of equivalents of the two salts which enter into the mixture.

In other words, the curve which has the indices for ordinates, and the equivalents for abscissæ, is a straight line. In this case it must be observed that the equivalent taken by the author is the quantity containing 1 equivalent of $SO_4.7HO$, namely 111. The author then gives a table containing the composition and equivalents of the salts examined, their indices as measured, and as calculated by the foregoing law, as well as the differences between observation and calculation. The law of variation of the index may be regarded as a consequence of

Gladstone's law; the refractive energy $\frac{n-1}{D}$ of a mixture of two bodies having no chemical action on one another, being the sum of the refractive energies of the components.

According to the author, isomorphous salts in crystallising together form mixtures analogous up to a certain point with liquid mixtures, in which the physical properties are the means of the properties of the component substances. This can, however, be regarded only as approximate, the distance of the molecules varying with the direction in double refracting crystals; in all cases, however, the approximation is comparable with that of the crystalline forms themselves. The author has also measured the angle of the optic axes in these crystals, and has calculated them by a formula given in the paper, but the results are not quite concordant. He hopes, however, by observations on the sulphates of zinc and magnesium, to establish a law for these perturbations, and so to connect more completely the optical properties of isomorphous salts with their crystalline form. J. M. T.

Optical Structure of Ice. By BERTIN (*Ann. Chim. Phys.* [2], 283—288).—A plate of ice, one centimeter thick, when placed in the polarising microscope, shows rings, provided that the plate is perpendicular to the axis of the crystal. If rings are not seen, it is necessary to use monochromatic light for illumination; regular fringes of oblique or parallel crystals will then be observed, or else irregular fringes of macled crystals. In the first case a suitable section in a direction perpendicular to the axis will give the rings; in the second a thin slice in Norremberg's apparatus—with parallel rays of light—gives a coloured mosaic, indicating a confused crystallisation.

The above method was employed to determine the structure of ice formed under various conditions. With icicles, and with the hoar-frost formed on windows, the crystals are irregular. Water frozen in a glass vessel in the open, forms crystals of ice at the side, which penetrate obliquely into the liquid, and finally reach the surface; when the film of ice thus formed has a thickness of some millimeters, it gives good rings, showing that the crystals have an axis perpendicular to the surface of the water. If the sides of the vessel are protected from the cold, ice is formed only on the surface: the axis is vertical, and it is therefore perpendicular to the cooling surface. To prove whether such is always the case, the following experiments were tried. Two rectangular wooden vessels, with a glass side in each, were employed; in one the glass was vertical, in the other it was placed at an angle of 45 degrees, *i.e.*, the normal exterior to this face was inclined 45 degrees to the horizon. They were filled with water and closed with a wooden cover, then exposed, with the glass to the north, on a cold day. After a few hours, the plates of ice were detached from the glass, and on examining the central portion, good rings were observed. In the first the axis was horizontal, in the second it was at an angle of 45 degrees to the horizon. In neither case was it vertical, but with both normal to the glass, *i.e.*, the cooling surface. A pan of water exposed to the cold forms a coating of ice on the top and bottom as well as on the sides.

The top and bottom coats have the axis vertical, whereas with those on the sides, it is perpendicular to the side. Hence the general law: *The axis of ice is perpendicular to the cooling surface.*

With ice prepared artificially, the crystals are formed irregularly, owing to the disturbed state of the liquid. R. C. W.

Note on a New Dioxide of Manganese Cell. By M. A. GAIFFE (*Compt. rend.*, lxxxvi, 728).—A porous carbon cylinder, pierced with holes parallel to its axes, serves both as one pole and as a porous vessel. In these holes are grains of dioxide of manganese. The other pole is a bar of zinc, which is placed with the carbon in a glass vessel containing an aqueous solution of 20 parts of zinc chloride in 100, made as neutral as possible. When the battery is in action, zinc oxide is formed, and falls as a powder to the bottom of the outer vessel. The advantages which this cell possesses as compared with ordinary dioxide of manganese cells are, 1, the double chloride of zinc and ammonium which usually incrusts the porous cell is not formed; 2, the attraction of the zinc chloride for water prevents evaporation. J. H. P.

Determination of Boiling Points. By A. HANDL and R. PRIBRAM (*Chem. Centr.*, 1878, 205—206).—The method is somewhat similar to that described by Jones (this Journal, 1878, Proc., 175). From 0·5 to 1 c.c. of the liquid under examination is placed in the closed limb of a small **U**-tube over a quantity of pure dry mercury. The **U**-tube is about 12 mm. internal diameter, and each limb is about 100 mm. in length. Both limbs are graduated from a common zero point. The temperature of the liquid is raised until a constant difference in the levels of the mercury in the two limbs is maintained. If a be the height of the mercury in the open limb, i the height in the closed limb, and b the barometric reading, then the tension of the vapour, e, for the observed temperature t, is—

$$e = b + a - i.$$

From a number of observations at different temperatures a series of tensions may be deduced, and from these the tension at 760 mm. may be calculated. M. M. P. M.

Absolute Boiling Points. By A. LADENBURG (*Deut. Chem. Ges. Ber.*, xi, 818—822).—A glass tube, from 1 to 4 mm. diameter, is half filled with the liquid to be experimented with, the air is carefully expelled, and after the tube has been sealed at the blowpipe, it is heated in a Bunsen's thermostat. The temperature is read off at a safe distance by means of a telescope, and the point at which the distinction between liquid and vapour ceases, or the point on cooling when a mist begins to form, is regarded as the absolute boiling point. The absolute boiling point of sulphur dioxide was found to be 157—161°, that of chlorine 148°, and ether 196°.

The critical point may be exhibited to a class by heating sulphur dioxide in a closed tube in aniline vapour. The experiment can be watched through a telescope or opera glass. W. C. W.

A Lecture Experiment and a Means of Quickly Evaporating Large Quantities of Liquid. By J. Brugnatelli (*Gazzetta chimica italiana*, viii, 16—21).—If water be heated in a tubulated receiver, with the neck placed vertically, and the tubulure closed until it boils equably and regularly, on opening the tubulure the column of vapour issuing from the vertical neck is greatly increased, and the liquid ceases to boil, the temperature sinking to 86—88°, if the source of heat be not too intense. Notwithstanding the diminution of temperature, the amount of liquid evaporated is largely increased (by about 50 per cent.), from the current of air carrying off the vapour as rapidly as it is formed.

By using large tubulated receivers with wide and long necks, and a good source of heat, very large quantities of liquid may be evaporated in a comparatively short time. The liquid should be kept nearly on a level with the tubulure by allowing it to flow in from a reservoir.

C. E. G.

On the Differences of Affinity of Chlorine, Bromine, and Iodine as Multiples of the same Constant. By R. Rühlmann (*Ann. Phys. Chem.* [2], iii, 461—464).—According to Thomsen, the quantities of heat given out in analogous chemical processes are either multiples of the same constant, or their differences are multiples of the same constant. This is very often found to be true, but often—probably through variations in the physical conditions—it is not the case. It is to be expected, when soluble compounds are formed, the constituents of which are themselves soluble in water without decomposition, that these variations of physical condition are most nearly compensated. Such compounds are formed by the union of the halogens with hydrogen and metals in water, the reaction being represented by $K + Cl + xH_2O$, where x is very large.

From Thomsen's numbers it appears that, except in the case of gold, the substitution of one atom of bromine for one atom of chlorine disengages 10,940 heat-units, and that the substitution of one atom of iodine for one atom of chlorine disengages 26,150 units. Now $10,940 = 2 \times 5,350$ nearly, and $26,150 = 5 \times 5,350$ nearly. From this it appears that the difference of the heats disengaged by chlorine and bromine is two-fifths of the difference of the heats disengaged by chlorine and iodine. The actual numbers for the various compounds do not stand in any simple relation to each other.

It may be noticed that two numbers frequently recurring in thermochemistry bear nearly a simple proportion to 5,350. We have $18,725 = \frac{7}{2} \times 5,350$, and $13,375 = \frac{5}{2} \times 5,350$, and these are numbers which have been observed by Thomsen as fundamental numbers.

J. H. P.

Relative Affinities and Reciprocal Displacements of Oxygen and the Halogen Elements in Metallic Compounds. By Berthelot (*Compt. rend.*, lxxxvi, 628—634).—This is a note to show that if the reactions of the different halogens and of oxygen are compared, and their reciprocal displacements studied, these depend, not on the type or atomic formula of the compound formed, but on the quantities of heat disengaged in the direct combination of the metals with each of the elements compared.

The following table gives the quantities of heat disengaged by each of several metals when united with oxygen, chlorine, gaseous bromine, or gaseous iodine, to form anhydrous compounds solid at ordinary temperatures:—

	O.	Cl.	Br.	I.
Potassium........	*69·8	104·6	99·0	85·2
Sodium	67·8	97·7	90·6	74·1
Calcium..........	65·7	84·8	75·6	59·1
Strontium........	65·7	92·3	83·5	67·0 nearly
Magnesium.......	†74·5 nearly	75·5	70·0 nearly	54·0 nearly
Manganese	†47·4 nearly	56·0	50·0 nearly	36·0 nearly
Iron (protosalts) ..	†34·1 nearly	41·0	50·0 nearly	36·0 nearly
Zinc	42·7	48·6	43·6	29·6
Cadmium	†32·8	46·6	41·7	27·5
Lead	25·1	41·4	36·2	25·2
Copper	20·4	32·9	29·0	21·7
Mercury..........	15·3	31·6	29·3	22·6
Silver............	3·0	29·4	26·7	19·2

According to this theory, if one of the four elements at the heads of the columns has a greater heat of combination with a metal than another of the four, it should replace it on combination with that metal. In every case in the table, the heat of combination of the metals with chlorine is greater than that with oxygen, and we should therefore expect that chlorine will always replace oxygen. This is verified by experience. The apparent exceptions, as in the case of manganese, where the chlorine may be displaced by oxygen, can be explained by the formation of oxides not equivalent to the chlorides decomposed. Gaseous bromine should also decompose nearly all the oxides. This usually occurs when the oxides are heated in the vapour of bromine. As with chlorine, the opposite reactions occur in certain cases, and even more easily. This we should expect, from the fact that the heat disengaged by bromine is always less than that disengaged by chlorine. With zinc, however, the numbers for bromine and oxygen are nearly equal. Accordingly we have the fact that a current of dry oxygen only incompletely displaces the bromine in $ZnBr_2$. The iodides furnish the best test of the theory, as their numbers are sometimes greater and sometimes less than those for the other corresponding compounds. With potassium and sodium, iodine should displace oxygen. This Gay-Lussac observed to take place at a dull red heat, although at a lower temperature the inverse reaction holds good, and iodate and periodate are formed. This is in accordance with theory, for the heat disengaged by the formation of the iodate from the iodide is greater than the difference between the numbers for the oxide and iodide, so that it goes to assist the displacement of some of the iodine by oxygen. With the metals of the alkaline earths oxygen displaces iodine, in confirmation of the theory. With lead and copper the numbers for the oxide and iodide are nearly equal, and here are

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* This number includes the formation of the hydrate and its union with water = 8 or 10.

† This number includes the formation of the hydrate = 1·2 to − 1·4.

found phenomena of equilibrium and dissociation, either element being able to replace the other according to their relative proportion. Iodine, as it should from the heat equivalent, easily displaces oxygen in combination with mercury and silver. The opposite reaction has not yet been observed. J. H. P.

Action of Oxygen on the Haloïd Compounds of Tin, Silicon, and Boron. By BERTHELOT (*Compt. rend.*, lxxxvi, 920—926).—In the formation of stannous oxide from its elements, 34·5 heat-units are evolved, and in the production of stannic oxide 67·6 units. In like manner the formation of stannous chloride produces 40·4, and stannic chloride 63·6 units. From these data we may conclude that oxygen will displace chlorine from stannous chloride if stannic oxide result, but that it will not decompose stannic chloride, inasmuch as the heat of formation of both compounds is almost identical. As the result of experiment, the former reaction was found to proceed according to the equations—

$$2SnCl_2 + O_2 = SnCl_4 + SnO_2 \text{ and } 2SnO + Cl_2 = SnCl_4 + SnO_2,$$

while a negative result was obtained in passing oxygen and stannic chloride through a red-hot porcelain tube, as theory had predicted.

It is true that Weber has stated that at a very high temperature chlorine is evolved by the action of SnO_2 on $SnCl_4$, but the author explains this by supposing that at such temperatures there is a tendency in the oxide to dissociate, when the formation of even a small quantity of stannous oxide would immediately entail the liberation of free chlorine. From considerations similar to the above, oxygen would be expected to displace bromine and iodine from the corresponding stannous and stannic salts. This conclusion was confirmed by experiment.

The data obtained in the investigation of the thermometric values of silicon and boron compounds also suggested theoretical results which it was found possible to carry out in practice. Oxygen ought in every instance to displace the halogens from their combinations with these elements, since the heat evolved in the union of silicon and boron with the halogens is much less than that evolved in their union with oxygen.

As a fact, silicon iodide takes fire in air, and Troost and Hautefeuille have shown that both silicon bromide and chloride, and boron bromide and chloride are decomposed when passed with oxygen through a red-hot tube, various oxy-compounds being formed, together with silica and boric anhydride in smaller proportion. J. W.

Suspension, Solution, and Chemical Combination. By W. DURHAM (*Chem. News*, xxxvii, 47).—Some time ago the author made some experiments on suspension of clay in water, in acid, and in saline solutions, which led him to experiment on various solutions, the results being very interesting, and promising to open up a line of research likely to lead to important facts as to the laws of solution and chemical affinity. The following conclusions may be drawn from the experiments undertaken:—

1. There seems to be a regular gradation of chemical attraction, from that exhibited in the suspension of clay in water up to that exhibited in the attraction of sulphuric acid for water, which we call chemical affinity.

2. That chemical combinations, solutions, and suspension differ only in one degree, and are manifestations of the same force, and definite chemical compounds are just the points where the affinity exerts force enough to hold an exact number of atoms with a certain strength.

3. The attraction of chemical affinity is not, in every case at least, exhausted when a definite compound is formed, but has sufficient power left to form solution or suspension compounds.

4. If chemical combination and solution are due to the same force, then solution will loosen the combination by spreading the affinity, and possibly there may be a rearrangement of the soluble matter and the solvent, analogous to what is known to take place when two salts having different acids and bases are mixed.

If these views prove to be correct, the author believes them to be able to explain many phenomena at present obscure. D. B.

Atomic Volume and Specific Gravity of Organic Compounds (*continued*). By R. HERMANN (*J. pr. Chem.* [2], xvii, 49—68).—This is a continuation of a former paper (*ibid.*, xiii, 365, and this Journal, 1876, ii, 496).

Atomic Volume and Specific Gravity of some Ketones.—The ketones of the hydrocarbons of the methane series consist of compounds which contain two univalent radicles, held together by the bivalent carbon-monoxide $\left(\frac{C}{1}\frac{O}{2}\right)$.

The radicles maintain the same atomic volume in the ketones as in the uncombined state.

Methyl-ketone (acetone), for example, has the formula, $\frac{C}{1}\frac{H_3}{1}-\frac{C}{1}\frac{O}{2}-\frac{C}{1}\frac{H_3}{2}$. Other ketones are—

Name.	Formula.	At. wt.	At. vol.	Cal. Sp. gr.	Obs. Sp. gr.
Ethyl-ketone	$\frac{C_2}{0{\cdot}75}\frac{H_5}{1}-\frac{C}{1}\frac{O}{2}-\frac{C_2}{0{\cdot}75}\frac{H_5}{1}$	86	105·0	0·819	0·815
Methyl-propyl-ketone	$\frac{C}{1}\frac{H_3}{1}-\frac{C}{1}\frac{O}{2}-\frac{C_3}{0{\cdot}66}\frac{H_7}{1}$	86	105·0	0·819	0·807

Haloïd Compounds of the Ketones.—In the substitution of hydrogen atoms of the ketones by the halogens, the latter assume the atomic volumes, $\frac{Cl}{0{\cdot}875}$, $\frac{Br}{1}$, $\frac{I}{1{\cdot}25}$, in the ortho-compounds.

When acetone is exposed to the action of chlorine gas, ortho-dichloracetone is formed, $\frac{C}{1}\frac{H_2}{1}\frac{Cl}{0{\cdot}875}-\frac{C}{1}\frac{O}{2}-\frac{C}{1}\frac{H_2}{1}\frac{Cl}{0{\cdot}875}$. Sp. gr. 1·236.

Phosphorus pentachloride acts upon acetone with formation of two different compounds—

(*a*.) Para-dichloracetone, $\frac{C}{1}\frac{H_3}{1} - \frac{C}{1}\frac{Cl_2}{0\cdot33} - \frac{C}{1}\frac{H_3}{1}$. Sp. gr. 1·47.

(*b*.) Meta-dichloracetone, $\frac{C}{0\cdot33}\frac{H_3}{1} - \frac{C}{0\cdot33}\frac{Cl_2}{0\cdot33} - \frac{C}{0\cdot33}\frac{H_3}{1}$. Sp. gr. 1·827.

The atomic volume of (*a*) is 78·16, of (*b*) 63·14.

By the energetic action of phosphorus pentachloride on acetone, therefore, not only is the oxygen of the carbonic oxide replaced by $\frac{Cl}{0\cdot33}$, but the atomic volume of the carbon is condensed from $\frac{C}{1}$ to $\frac{C}{0\cdot33}$. As, however, the grouping of the elements of the acetone remains unaltered, meta-dichloracetone when heated with water at 180° re-forms acetone, the carbon changing its atomic volume by the absorption of heat from $\frac{C}{0\cdot33}$ to $\frac{C}{1}$, and $\frac{C}{0\cdot33}\frac{Cl}{0\cdot33}$ by exchange with the elements of water becoming converted into $\frac{C}{1}\frac{O}{2}$. This process indicates a method of condensing the atomic volume of C, and restoring it again to its normal state without destroying the original constitution of the organic compound.

Atomic Volume and Specific Gravity of the Aldehydes.—In the formation of acetaldehyde from ethane alcohol, $\frac{O}{1\cdot5}$ is converted into $\frac{O}{3}$ with absorption of heat. This large atomic volume of oxygen explains the unstability of these compounds.

Acetal is formed by the combination of acetaldehyde with two atoms of ethane-alcohol and separation of one atom of water. Its formula is $\frac{C_6}{0\cdot75}\frac{H_{14}}{1}\frac{O_2}{2}$.

The $\frac{O}{3}$ of the aldehyde and $\frac{O_2}{1\cdot5}$ of the alcohol become changed into $\frac{O_2}{2}$ of the ethal and $\frac{O}{1}$ of water, while five units of heat are absorbed by the ethal and one is set free.

Phosphorus pentachloride reacts on acetaldehyde with formation of orthaldehyde chloride $\frac{C_2}{0\cdot75}\frac{H_4}{1}\frac{Cl_2}{0\cdot75}$, which must not be confounded with $\frac{C_2}{1}\frac{H_4}{1}\frac{Cl_2}{0\cdot75}$.

The atomic volumes of aldehyde, paraldehyde, acetal, and aldehyde chloride are respectively 56 : 44·75 : 144·75 : 81.

Magnitude of the Atomic Volume of the elements contained in Organic Compounds, and the varying Valency of Carbon.—The only elements concerned are H, C, O, N.

The atomic volume of hydrogen does not vary, and it is $6{\cdot}5 = \frac{\mathrm{H}}{1}$.

Hence it follows that the atomic volume of water being 18, the normal atomic volume of oxygen $\left(\frac{\mathrm{O}}{1}\right)$ is 5·0, for $2 \times 6{\cdot}5 = 13$, and $18 - 13 = 5$.

From the specific gravity of liquid ammonia, 0·629, it follows that the atomic volume of ammonia is $\frac{17}{0{\cdot}629} = 27$, and therefore the normal atomic volume of nitrogen is 7·5, for $3 \times 6{\cdot}5 = 19{\cdot}5$, and $27 - 19{\cdot}5 = 7{\cdot}5$.

Carbon possesses the peculiarity of not being able to exceed the atomic volume of $\frac{\mathrm{C}}{1} = 7{\cdot}5$.

Normally carbon $\frac{\mathrm{C}}{1}$ is possessed of four affinities, but these may be reduced by pairing.

The following modifications have been observed, $\frac{\mathrm{C}}{0{\cdot}33}$; $\frac{\mathrm{C}}{0{\cdot}5}$ bivalent; $\frac{\mathrm{C}}{1}$ quadrivalent; $\frac{\mathbf{C}}{1}$ bivalent; $\frac{\text{Ꞓ}}{1}$ univalent; $\frac{\text{Ꞓ}}{0{\cdot}875}$ univalent; $\frac{\text{Ꞓ}}{0{\cdot}5}$ univalent.

In addition to these there are the inorganic carbons, $\frac{\mathrm{C}}{0{\cdot}66}$ graphite, and $\frac{\mathrm{C}}{0{\cdot}44}$ diamond, the valency of which is yet unknown.

The atomic volume of oxygen in organic compounds varies between $\frac{\mathrm{O}}{0{\cdot}5}$ and $\frac{\mathrm{O}}{3}$. $\frac{\mathrm{O}}{3}$ is found in the aldehydes; $\frac{\mathrm{O}}{2}$ in the ethers and fatty acids; $\frac{\mathrm{O}}{1{\cdot}5}$ in the alcohols; $\frac{\mathrm{O}}{1}$ in water and metallic oxides of the formula RO; $\frac{\mathrm{O}}{0{\cdot}5}$ in the hydroxyl of the alcohols of the higher acids, and in the oxybenzoic acids.

The atomic volume of nitrogen varies between $\frac{\mathrm{N}}{3}$ and $\frac{\mathrm{N}}{0{\cdot}33}$. $\frac{\mathrm{N}}{3}$ is contained in liquid cyanogen and prussic acid. $\frac{\mathrm{N}}{1}$ is found in ammonia and several other compounds. $\frac{\mathrm{N}}{0{\cdot}33}$ occurs in urea. The facility with which nitrogen takes up varying quantities of latent heat and parts with it again gives it peculiar properties, which are important from a physiological stand-point. $\frac{\mathrm{N}}{3}$ is contained in the poisonous prussic acid, and possibly in the poisonous alkaloïds. In urea, which contains $\frac{\mathrm{N}}{0{\cdot}33}$, the power of nitrogen to support animal life is exhausted;

but urea promotes vegetable life, and becomes converted into ammonium carbonate, which contains $\frac{N}{1}$.

Atomic Volume and Specific Gravity of the Hydrocarbons of the Ethylene Series, and some of their Derivatives.—Since ethylene has the formula $\frac{C_2}{1}\frac{H_4}{1}$, its homologues being compounds of $\frac{C_2}{1}\frac{H_4}{1}$, with the bivalent $\frac{C}{1}\frac{H_2}{1}$, have the general formula $\frac{C_n}{1}\frac{H_{2n}}{1}$.

The hydrocarbons of this series produce condensation of the halogens to a greater extent than those of the methane series; thus, Cl, Br, I become (α) in combination $\frac{Cl}{0{\cdot}75}\frac{Br}{1}\frac{I}{1{\cdot}5}$; ($\beta$) on substitution $\frac{Cl}{1}\frac{Br}{1{\cdot}25}\frac{I}{0{\cdot}5}$. The following table gives a few of the ethylene series and their derivatives:—

Name.	Formula.	At. wt.	At. vol.	Calculated. Sp. gr.	Observed. Sp. gr.
Ethylene	$\frac{C_2}{1}\frac{H_4}{1}$	28	41	0·683	0·674
Propylene	$\frac{C_3}{1}\frac{H_6}{1}$	42	61·5	0·683	0·683
Ethylene chloride	$\frac{C_2}{1}\frac{H_4}{1}\frac{Cl}{0{\cdot}75}$	99	78·5	1·261	1·271
Allylene chloride	$\frac{C_3}{1}\frac{H_6}{1}\frac{Cl}{0{\cdot}75}$	113	99	1·141	1·165
Ethylene alcohol	$\frac{C_2}{1}\frac{H_4}{1}\frac{O}{1{\cdot}5}$	44	48·5	0·907	0·898
Acrylic acid	$\frac{C_6}{1}\frac{H_6}{1}\frac{O_3}{2}+\frac{H_2}{1}\frac{O}{1}$	144	132	1·090	1·090
Allylene ether	$\left(\frac{C_3}{1}\frac{H_5}{1}\right)_2\frac{O}{2}$	98	120	0·816	—

Atomic Volume and Specific Gravity of the Acetylene-hydrocarbons and their Derivatives.—These hydrocarbons fall into two groups—

(α.) Polymeric acetylene-hydrocarbons.

(β.) Substituted benzene-hydrocarbons.

The polymeric acetylene-hydrocarbons are saturated compounds of the formula $\frac{\text{Ꞓ}_n}{1}\frac{H_{2n}}{1}$. The following table contains a few of them as well as some substituted benzene-hydrocarbons:—

Name.	Formula.	At wt.	At vol.	Calculated Sp. gr.	Observed Sp. gr.
Acetylene..	$\frac{\text{Ꞓ}_2}{1}\frac{H_2}{1}$	26	28	0·928	—
[illegible]..	$\frac{\text{Ꞓ}_6}{1}\frac{H_6}{1}$	78	84	0·928	0·899

Name.	Formula.	At. wt.	At. vol.	Calculated Sp. gr.	Observed Sp. gr.
Toluene ..	$\frac{\Theta_6}{1}\frac{H_5}{1}-\frac{C}{1}\frac{H_3}{1}$	92	104·5	0·880	0·882
Cumene ..	$\frac{\Theta_6}{1}\frac{H_5}{1}-\frac{C_3}{0\cdot66}\frac{H_7}{1}$	120	138·0	0·872	—

Benzene-haloïds.—Orthochlorobenzene is formed when chlorine acts on benzene mixed with iodine, metachlorobenzene when iodine is not present. In the first case the chlorine assumes the atomic volume $\frac{Cl}{0\cdot875}$, in the second case the chlorine atoms are condensed, and para- and meta-chlorobenzene are formed.

The atomic volumes of bromine and iodine when they act on benzene are $\frac{Br}{1}\frac{O}{1\cdot25}$.

Substitution-product of benzene with NO_2.—Nitrobenzene has the formula $\frac{\Theta_6}{1}\frac{H_5}{1}-\frac{N}{1}\frac{O_2}{1\cdot5}$.

Atomic weight, 123; specific gravity, 1·20; atomic volume, 102·5.

Substitution-product with HO.—This is phenol, and the hydroxyl is $\frac{H}{1}\frac{O}{1\cdot5}$.

Substitution-product with CHO.—Benzoic aldehyde, the formula of which is $\left(\frac{\Theta_6}{1}\frac{C}{1}\right)\frac{H_6}{1}\frac{O}{2}$

Substitution products with CHO_2.—These are benzoic, toluic, mesitylenic, and cumic acids.

The constitution of the first and last is as follows:—

Name.	Formula.	At. wt.	At vol.	Calculated. Sp. gr.
Benzoic acid ..	$\left(\frac{\Theta_{12}}{1}\frac{C_2}{1}\right)\frac{H_{10}}{1}\frac{O_3}{1}+\frac{H_2}{1}\frac{O}{1}$	244	203·4	1·202
Cumic acid	$\left(\frac{\Theta_{12}}{1}\frac{C_8}{1}\right)\frac{H_{22}}{1}\frac{O_3}{1}+\frac{H_2}{1}\frac{O}{1}$	328	326	1·006

Anilides.—These compounds contain a peculiar modification of carbon $\frac{C}{0\cdot875}$, which is possibly the cause of their fine colours.

Ethereal Oils of the Formula $C_{10}H_{16}$.—Oil of turpentine, terebene, oil of citron. The composition of oil of turpentine is given as—

$$\left(\frac{\Theta_6}{1}\frac{H_4}{1}-\frac{C_3}{0\cdot66}\frac{H_7}{1}-\frac{C}{1}\frac{H_3}{1}\right)+\frac{H_2}{1}\text{ or }\left(\frac{\Theta_6}{1}\frac{H_4}{1}\right)-\left(\frac{C_2}{0\cdot75}\frac{H_5}{1}\right)_2+\frac{H_2}{1}.$$

Both formulæ correspond with 10 atoms of carbon, 16 of hydrogen, and 25 units of heat.

The different distribution of the heat-units causes a difference in the grouping of the atoms, and hence a difference in the properties of the compounds, which are in other respects similarly constituted.

G. T. A.

On the Velocity of Molecules. By F. WÄCHTER (*Liebig's Annalen*, cxci, 309—320).—The object of this paper is to show that the velocities of molecules, which hitherto have been arrived at only by mathematical developments of the theory of heat, may be determined approximately by a purely empirical method, whereby at the same time theoretical results are subjected to the test of experiment.

The method adopted by the author is based upon the proposition that *the true specific heats of equal weights of different substances are proportional to the squares of the mean velocities of their molecules*, which is a necessary consequence of the hypothesis that heat is nothing more than the *vis viva* of the smallest particles of bodies. Putting w and w_1 for the true specific heats of two substances, m and m_1 for their masses, and u and u_1 for the velocities of their molecules—

$$w : w_1 = m\,u^2 : m_1\,u_1^2.$$

When $m = m_1$, that is, when equal weights of the two substances are considered, $w : w_1 = u^2 : u_1^2$. This formula is applicable to solids and liquids, as well as to gases.

For example, the specific heat of platinum between 0° and 100° = 0·0319. Assuming this to be the true specific heat between − 273° and 0°, it follows that 1 kilogram of platinum requires, in order to raise it from − 273° to 0°, 8·7085 units of heat, the mechanical equivalent of which is $8·7085 \times 424 = 3692·4$ kilogram-meters. This number, according to the above proposition, is the square of the mean velocity of the atoms of platinum at 0°: hence the velocity, u, = 60·7 meters. The same calculation applied to other metals gives for palladium, $u = 82·9$; for iron, $u = 113·8$; for silver, $u = 80·4$ meters.

But the squares of the velocities of the atoms at equal temperatures are inversely proportional to their masses, or the velocities are proportional to the square roots of the masses, and therefore to the square roots of the atomic weights, so that $u = \sqrt{\frac{m\,u^2}{m_1}}$. Hence the velocity of the platinum atom may be calculated from that of the palladium atom. Thus, ssubtituting for u the velocity of the palladium atom as calculated above (82·9 meters), and for m and m_1 the atomic weights of palladium (106·5) and platinum (197·4), the velocity, u, of the platinum atom is found to be 60·8 meters. Similarly, taking iron ($u = 113·8$ meters, $m = 56$) and silver ($u = 80·4$, $m = 108$) instead of palladium, the velocity of the platinum atom = 60·4 and 59·6 meters respectively.

These examples serve to show that it is possible to deduce approximately the mean specific heat of ice between − 273° and 0° from that of a metal, such as platinum, whose specific heat at known temperatures varies but slightly. Thus, from the velocity of platinum at 0° (60·7 meters), the atomic weight of platinum (197·4), and the molecular weight of water (9), the velocity of the ice molecule at 0° is found to be 284·5 meters. But $\frac{284·5^2}{424} = 191·06$ is the number of units of heat required to raise a kilogram of ice from − 273° to 0°; whence it follows that the mean specific heat of ice = 0·7. The total heat required to convert a kilogram of ice at − 273° into steam at 100° will therefore be as follows:—

To heat the ice from − 273 to 0°....	191·06	units
To melt the ice	79·25	„
To heat the water from 0° to 100° ..	100·50	„
To evaporate the water............	536·50	„
Total ..	907·31	„

The mechanical equivalent of this heat is 907·31 × 424 = 384699·44 kilogram-meters. Now, since it is a matter of indifference, as regards the amount of work done, whether a kilogram of water moves as a whole in a given direction and with a certain velocity, or whether each separate molecule moves in any direction with the same velocity, the number 384699·44 is the square of the velocity of the molecule of steam at 100°: hence the velocity, *u*, is 620·2 meters. Clausius gives for the velocity of steam at 0°, 614 meters, which according to the author corresponds to a velocity at 100° of 626·94 meters, a number differing but little from that found above.

On the same principle the author has calculated the heat of evaporation of mercury (70·61 units), the heat of liquefaction of bromine (27·59 units), and the mean specific heat of liquid iodine (0·17).

J. R.

Naumann's Method of Determining Molecular Weights. By H. Kopp (*Deut. Chem. Ges. Ber.*, xi, 689—692).—This is a paper continuing the controversy as to the significance of Naumann's distillation method (this volume, 47, 138, 263, 283). Naumann himself considers that the molecular weights rather than the vapour-densities of bodies are determined, and this notwithstanding that Horstmann affirms the contrary (this volume, 467).

The author believes that the method gives, for the two liquids, if their vapour-tensions at the temperature of distillation are known, only the relation between their vapour-densities as they exist in the mixed vapour. He refers at some length to a paper by Wanklyn (*Proc. Roy. Soc.*, xii, 534; *Ann. Chem. Pharm.*, cxxviii, 328), and one by Berthelot (*Compt. rend.*, lvii, 430; *Ann. Chem. Pharm.*, cxxviii, 321) on this subject.

T. C.

Inorganic Chemistry.

Amidosulphonic Acid. By E. Berglund (*Bull. Soc. Chim.* [2], xxix, 422—426).—The author has succeeded in preparing this acid by decomposing (1) the basic barium salt, or (2) the barium and mercury salt of imidosulphonic acid with dilute sulphuric acid, and boiling the product with baryta-water. The reactions are thus represented:—

1. $N_2Ba_3(SO_3)_4 + H_2SO_4 = BaSO_4 + 2[Ba(SO_3)_2NH]$;
   $Ba(SO_3)_2NH + H_2O = NH_2SO_3H + BaSO_4$.
2. $N_2HgBa_2(SO_3)_4 + 2H_2SO_4 = 2BaSO_4 + N_2HgH_4(SO_3)_4$;
   $N_2HgH_4(SO_3)_4 + 2H_2O = 2NH_2SO_3H + H_2SO_4 + HgSO_4$.

Pure amidosulphonic acid is best obtained by decomposing the silver salt with hydrogen sulphide, and evaporating the solution over sulphuric acid. It forms large transparent crystals, which are anhydrous and permanent in the air, and may be heated to 190° without undergoing decomposition. It dissolves easily in water and with difficulty in alcohol. The aqueous solution may be heated to the boiling point without alteration, but the acid is converted into acid ammonium sulphate on prolonged boiling. This reaction takes place more rapidly in presence of hydrochloric acid, and is determined at once by addition of potassium chlorate or nitrous acid, even in the cold. The aqueous solution dissolves iron and zinc, evolving hydrogen, and forming the corresponding amidosulphonates. It gives no precipitates with barium hydrate, but when heated with hydrochloric acid and barium chloride, it gradually deposits barium sulphate; whilst with potassium chlorate and hydrochloric acid in presence of barium chloride, it gives at once a precipitate of barium sulphate on being heated. These reactions are characteristic of the acid.

The salts of amidosulphonic acid are all soluble in water, but insoluble in alcohol, and generally crystallise well. Their solutions may be heated to ebullition, without alteration. The salts containing water of crystallisation undergo decomposition at 100°, yielding sulphates; the anhydrous salts are stable at higher temperatures. The salts of the alkalis give off ammonia at 160—170°, being converted into salts of imidosulphonic acid. The following have been analysed:—

Potassium salt, NH_2SO_3K.—Obtained by double decomposition of the barium salt and potassium sulphate. Rhombic tables.

Sodium salt, NH_2SO_3Na.—Very soluble needles.

Lithium salt, NH_2SO_3Li.—Long, deliquescent needles.

Ammonium salt, $NH_2SO_3NH_4$.—Large, deliquescent tables, melting without decomposition at 125°.

Thallium salt, NH_2SO_3Tl.—Long, brilliant prisms.

Silver salt, NH_2SO_3Ag.—Long, hard prisms, dissolving in 15 parts of water at 19°, and blackening in the light.

Barium salt $(NH_2SO_3)_2Ba$.—Fine, long prisms, soluble in three parts of water at the ordinary temperature.

Strontium salt $(NH_2SO_3)_2Sr + 4H_2O$.—Large, well-formed prisms, more soluble than the barium salt.

Calcium salt $(NH_2SO_3)_2Ca + 4H_2O$.—Thin laminæ, very soluble.

Lead salt $(NH_2SO_3)_2Pb + H_2O$.—The most soluble of the amidosulphonates. Small needles, not deliquescent.

Nickel salt $(NH_2SO_3)_2Ni + 3H_2O$.—Clusters of emerald-green needles, very soluble.

Cobalt salt $(NH_2SO_3)_2Co + 3H_2O$.—Stellate groups of red needles.

Manganese salt $(NH_2SO_3)_2Mn + 3H_2O$.—Crystalline, rose-red mass; very soluble.

Zinc salt $(NH_2SO_3)_2Zn + 4H_2O$.—Radiated crystalline mass.

Cadmium salt $(NH_2SO_3)_2Cd + 5H_2O$.—Very soluble microscopic tables.

Copper salt $(NH_2SO_3)_2Cu + 2H_2O$.—Blue needles and long tables, less soluble than the preceding salts.

The magnesium, aluminium, and uranium salts are very soluble. The ferric salt is resolved on evaporation into basic salt and free acid. J. R.

The Flame Reaction of Boric Acid as a Lecture Experiment. By H. GILM (*Deut. Chem. Ges. Ber.*, xi, 712—713).—A regularly tinted and beautiful green boric acid flame is best obtained by passing the vapour of boric ether through a kind of Bunsen burner, made by enclosing a small, narrow, glass tube in a vertical one, so that the gas may mix with air previous to ignition at the upper end of the tube. The same result is obtained by allowing the vapour of the ether to pass through an ordinary Bunsen burner, the tube of which is heated to avoid condensation. For qualitative analysis it is most convenient to use a small flask, provided with a cork, through which passes a short, drawn out glass jet, a wider tube being placed over the latter, and the gas ignited at the top. After the addition of hydrochloric acid, very small quantities of boric acid may be detected by this means. T. C.

Crystallisation of Silica in the Dry Way. By P. HAUTEFEUILLE (*Compt. rend.*, lxxxvi, 1133).—G. vom Rath in 1868 discovered in trachyte a new form of crystallised silica, which he called tridymite, and Rose subsequently found that when amorphous silica was kept for some time in fused microcosmic salt, it was converted into tridymite. The author in this paper shows that an alkaline tungstate may be advantageously substituted for microcosmic salt.

When amorphous silica is kept for some hours in tungstate of soda, at the melting point of silver, it is converted into tridymite, but if the temperature rises above 100° C., the silica is attacked by the alkaline tungstate, forming a silicate, which, when the temperature falls again, is reconverted into tridymite. C. W. W.

Behaviour of Phosphorus with various Metallic Solutions. By R. BÖTTGER (*Chem. Centr.*, 1878, 208).—Pure phosphorus precipitates gold, copper, and palladium from solutions of the salts of these metals; silver is thrown down as phosphide, whilst platinum, uranium, nickel, iron, zinc, cadmium, and cobalt are not precipitated by phosphorus. M. M. P. M.

Vapour-density of Ammonium Sulphide. By G. SALET (*Compt. rend.*, lxxxvi, 1080).—No contraction takes place when sulphuretted hydrogen and ammonia gas are mixed together, at a temperature of 80°; this shows that the statement that a molecule of ammonium sulphide in the state of vapour occupies the same volume as an alcoholic sulphide is incorrect. The apparatus employed is fully described. W. C. W.

Composition of Ancient Glass and Crystal. By E. PELIGOT (*Ann. Chim. Phys.* [5], xiii, 271—283).—It is generally stated that the glass manufactured by the ancients was prepared from the same materials as are used at the present time. Such is not, however, the author's opinion; common glass and lead crystal had formerly a composition very different from that of more recent date. Three ingredients are now employed in the manufacture of glass, namely, silica, soda, and lime. Bohemian glass has potash substituted for the soda. But with antique glass only two substances were employed, sand and an alkaline flux. Many old recipes are given, but no mention is made of lime; this substance, however, is generally present, and was probably introduced accidentally with the flux or the sand. Analyses of various selected specimens of ancient glass, chiefly from Autun, of about the 11th century, gave:—Silica, 66·0—70·9; lime, 5·8—7·9; alumina, oxides of iron, and manganese, 2·8—5·7; soda and potash, 16·7—24·7. The presence of soda together with potash, indicates that the ash of seaweed was used as a flux. Lime has only recently been employed in the manufacture of glass. Window glass analysed by Dumas 35 years ago contained only 3·8 per cent. of lime. Water and chemical reagents have considerable action upon ancient glass. A well made glass at the present time contains 12—15 per cent. of lime; the alkalis are contained in almost equivalent proportions. These data furnish a ready method for distinguishing modern from ancient glass.

Lead Crystal.—Very old specimens of glass are found to contain lead, but the author does not regard them as real crystal. This material is of modern manufacture, introduced by the English, under the name of "flint-glass." R. C. W.

The Equivalent of Gallium. By LECOQ DE BOISBAUDRAN (*Compt. rend.*, lxxxvii, 941—943).—The equivalent was determined —1. By igniting gallium-ammonium alum. 2. By igniting the nitrate obtained from a known weight of metal.

The alum was prepared from metallic gallium, and was freed by repeated crystallisation from the traces of copper and zinc which this element is apt to contain. 3·1044 grams gave on ignition 0·5885 of oxide, the composition of the latter corresponding with that of the sulphate originally present; from these numbers the equivalent 70·032 is deduced.

The metal used in the preparation of the nitrate did not show in the spectroscope any lines foreign to gallium. ·4481 gram yielded after conversion into nitrate and ignition, 0·6024 gram of oxide, which gives the number 69·698 for the equivalent.

The mean of these two experiments, 69·865, may be taken as a fair approximation to the truth, considering the small quantity of material at the disposal of the operator.

The author points out the coincidence which exists between the experimental equivalent and the numbers which he has calculated from theoretical data for a body intermediate between aluminium and indium. The maximum theoretical equivalent would be 69·97; the minimum, 69·66; and the mean, 69·82; the latter, as will be seen, scarcely differs from that actually obtained; it is, however, a little higher than that adopted by Mendelejeff, for the element which in his classification should correspond with gallium. J. W.

Compounds of Didymium and Lanthanum. By F. FRERICHS and F. SMITH (*Liebig's Annalen*, cxci, 331—366).—The authors have prepared and analysed a large number of salts of didymium and lanthanum, which they regard as triatomic metals, in accordance with the specific heats determined by Bunsen and Hillebrand (*Pogg. Ann.*, clviii, 71). They obtained from cerite a mixture of the oxides of the metals, from which by further treatment pure didymium and lanthanum salts were isolated. No process for the complete separation of the two elements has yet been discovered. The methods adopted by the authors are given in detail.

DIDYMIUM COMPOUNDS (*Di* = 144).—*Chloroplatinate*,

$2DiCl_3.3PtCl_4.24H_2O$.

Obtained by mixing concentrated solutions of didymium chloride and platinic chloride. Very fine orange-coloured tables.

Chloro-aurate, $2DiCl_3.3AuCl_3.21H_2O$.—Brilliant yellow tables, very hygroscopic and deliquescent.

Oxychloride, $DiOCl$.—Obtained by heating didymium oxide in chlorine. Resolved by boiling with water into hydrate and chloride.

Didymium and Zinc Bromide, $2DiBr_3.3ZnBr_2.36H_2O$.—Reddish-brown needles, very hygroscopic, taking up water even from calcium chloride.

Didymium and Nickel Bromide, $2DiBr_3.3NiBr_2.18H_2O$. — Small brownish crystals, which rapidly absorb water from the air.

Didymium and Zinc Iodide, $2DiI_3.3ZnI_2.24H_2O$.—Small yellowish needles, very hygroscopic.

Fluoride, $2DiF_3.(HF)_3$.—Thrown down as a gelatinous precipitate on adding hydrofluoric acid to a solution of didymium sulphate. Over the water-bath it dries up to a transparent rose-coloured mass.

Di_4O_9.—An oxide having this composition was obtained as a chestnut-brown powder by decomposing the nitrate at a gentle heat, and then heating the residual oxide to low redness in a current of oxygen. It dissolves in nitric acid, giving off oxygen.

Sulphide, Di_2S_3.—A yellow or brownish substance, obtained by heating the oxide in vapour of carbon bisulphide. It dissolves easily in acids, giving off hydrogen sulphide.

Nitrate, $DiO_3(NO_2)_3.6H_2O$.—Large violet crystals having this composition are obtained by dissolving the oxide in nitric acid and evaporating the solution over sulphuric acid. The salt absorbs water from the air, becomes anhydrous at 200°, and melts without decomposition at 300°. It dissolves easily in alcohol. Forms crystalline compounds with other nitrates.

Didymium and Zinc Nitrate, $2DiO_3(NO_2)_3.3ZnO_2(NO_2)_2.69H_2O$.—Deliquesces extremely rapidly in the air.

Didymium and Nickel Nitrate, $2DiO_3(NO_2)_3.3NiO_2(NO_2)_2.36H_2O$.—Large bright-green tables, hygroscopic and very easily soluble in water.

Didymium and Cobalt Nitrate, $2DiO_3(NO_2)_3.3CoO_2(NO_2)_2.48H_2O$.—Dark-red crystals, obtained with great difficulty. Very soluble.

Hypochlorite, $Di(OCl)_3$.—Obtained by passing chlorine into water in which didymium hydrate is suspended. Thin nearly colourless tables, dissolving sparingly in water, but easily in strong acids.

Basic Sulphate $[Di_2(OH)_3]_2.(SO_4)_3$.—Ammonia added to the neutral sulphate throws down a gelatinous precipitate which dries up to a mass having this composition. The salt is insoluble in water, but easily soluble in acids.

Neutral Sulphate, $Di_2(SO_4)_3$.—This salt crystallises from strongly acid solutions in rose-red crystals containing $6H_2O$, and from neutral saturated solutions on slow evaporation in crystals containing $9H_2O$. The latter give off two-thirds of their water at 200°.

Selenate, $Di_2(SeO_4)_3.6H_2O$.—Fine rose-red prisms, very easily soluble in water, obtained by evaporating a solution of the oxide in selenic acid.

Selenite, $Di_2(SeO_3)_3.6H_2O$.—Obtained as a gelatinous precipitate on adding alcohol to a mixture of concentrated solution of didymium nitrate with selenious acid.

Phosphate, $DiPO_4.H_2O$.—Obtained by boiling solutions of didymium with phosphoric acid, or by adding trisodium phosphate to didymium sulphate. Insoluble in water; soluble in acids.

Triphosphate, $Di_2(HO_3PO)_3$.—Precipitated from the sulphate by disodium phosphate.

Pyrophosphate, $Di_2(H_2O_4P_2O_3)_3$.—Precipitated by neutral sodium pyrophosphate from acid solutions of didymium. Soluble in excess of the precipitant.

Metaphosphate, $DiO_3(PO_2)_3$.—Rose-red powder, precipitated by sodium metaphosphate from didymium sulphate.

Arsenate, $Di_2(H.O_3.AsO)_3$.—Pale-red precipitate thrown down by disodium arsenate from didymium sulphate. Insoluble in water.

Phosphite, $Di_2(O_2.PHO)_3$.—Precipitated from solutions of didymium by disodium phosphite.

Arsenite, $Di(O_2.AsHO)_3$.—A white granular powder, insoluble in water, formed by boiling didymium hydrate with aqueous solution of arsenious acid.

Chromate, $Di_2(O_2.CrO_2)_3$.—A yellow granular powder, precipitated by potassium bichromate from didymium sulphate. Dissolves sparingly in water, easily in dilute acids.

Manganate, $Di_2(O_2.MnO_2)_3$.—Formed by heating didymium nitrate with manganese dioxide. Black powder, insoluble in water, soluble with dark-red colour in sulphuric acid.

Permanganate, $Di(MnO_4)_3.21H_2O$.—Deposited from a mixture of potassium permanganate and didymium sulphate on standing. Reddish-brown crystalline powder, sparingly soluble in water.

Borate, $Di_2(O_2B_4O_5)_3$.—Thrown down as a white gelatinous precipitate on adding sodium borate to a solution of didymium sulphate. Insoluble in water.

Molybdate, $DiH_3O_6(MoO_2)_3$.—Obtained as a pale-red gelatinous precipitate by adding ammonium molybdate to solutions of didymium.

Tungstate, $Di_2(O_2WoO_2)_3$.—Precipitated by disodium tungstate from didymium sulphate. Gelatinous precipitate, drying up to a rose-red mass, insoluble in water.

Lanthanum Compounds ($La = 139{\cdot}2$).—The following bodies were obtained in the same manner as the corresponding didymium compounds, which in general they closely resemble.

Chloroplatinate, $2LaCl_3.3PtCl_4.24H_2O$.

Chloro-aurate, $2LaCl_3.3AuCl_3.21H_2O$.

Oxychloride, $LaOCl$.—When boiled with water containing didymium oxychloride in suspension, it is gradually converted into lanthanum chloride.

Lanthanum and Zinc Bromide, $2LaBr_3.3ZnBr_2.39H_2O$ (?).

Lanthanum and Nickel Bromide, $2LaBr._3.3NiBr_2.18H_2O$.

Lanthanum and Zinc Iodide, $2LaI_3.3ZnI_2.27H_2O$.

Fluoride, $2LaF_3.(HF)_3$.

Sulphide, La_2S_3.

Lanthanum and Zinc Nitrate, $2LaO_3(NO_2)_3.3ZnO(NO_2)_2.69H_2O$.

Lanthanum and Nickel Nitrate, $2LaO_3(NO_2)_3.3NiO(NO_2)_2.36H_2O$.

Basic Sulphate, $[La_2(OH)_3]_2(SO_4)_3$.

Neutral Sulphate, $La_2(SO_4)_3.6H_2O$.

Selenate, $La_2(SeO_4)_3.12H_2O$.

Selenite, $La_2(SeO_3)_3.9H_2O$.

Phosphate, $LaO_3{\cdot}PO$.

Pyrophosphate, $La_2(H_2O_4.P_2O_3)_3$.

Triphosphate, $La_2(HO_3.PO_3)_3$.

Metaphosphate, $LaO_3.(PO_2)_3$.

Arsenate, $La_2(HO_3AsO)_3$.

Phosphite, $La_2(O_2PHO)_3$.

Arsenite, $La_2(O_2AsHO)_3$.

Chromate, $La_2(O_2CrO_2)_3$.

Manganate, $La_2(O_2MnO_2)_3$.

Permanganate, $LaO_3(MnO_3)_3.21H_2O$.

Borate, $La_2(O_2B_4O_5)_3$.

Molybdate, $LaH_3O_6(MoO_2)_3$.

Tungstate, $La_2(O_2WO_2)_3$.

Cyanide, $La(CN)_3$.—Obtained as a gelatinous precipitate by adding potassium cyanide to a solution of lanthanum sulphate. Forms double salts with other cyanides.

J. R.

Presence of Oxygen in Bessemer Metal. By S. Kern (*Chem. News*, xxxvii, 48).—The following experiment was made. 1000 grams of the Bessemer metal, taken out of the retort just before the addition of spiegeleisen, was cast in a small cast-iron mould. The casting was divided into two pieces, one of them being hammered strongly in the heated state, whilst the other was allowed to cool. The two specimens were then tested for oxygen by the method formerly described by the author.

The following results were obtained :—

	Expt. 1.	Expt. 2.
Hammered specimen	·165	·162
Not hammered ditto	·185	·171

The quantity of oxygen in steel naturally depends upon the time the blowing process is continued after the carbon of the metal in the converter has been consumed. Britton found ·76 gram of oxygen in steel. Such metal which may be called burnt steel, is of course not suitable for manufacturing purposes. D. B.

Some Reactions of Silver Chloride and Bromide. By M. C. LEA (*Am. J. Sci.* [3], xv, 189—191).—The author's former results, as also those of von Bibra, are confirmed: it is now established that the substance produced by the action of light on silver chloride is of a much more permanent character than that formed in the case of the other silver haloïds, inasmuch as nitric acid decomposes the bodies so produced from silver bromide and iodide (with formation of silver, and ordinary silver bromide and iodide), but is without action on the substance formed from silver chloride.

The author finds that after five days' action of strong sunshine on moist silver chloride, exposed in a thin layer and frequently stirred up, about one per cent. of the chloride is acted upon. The darkened chloride is not acted on by nitric acid sp. gr. 1·28 in the cold, so that it does not contain reduced silver, but as it is quickly whitened by *aqua regia*, it is probable that the darkening is due to the formation of a subchloride or oxychloride. By digesting the darkened chloride (precipitated in presence of hydrochloric acid) with nitric acid of sp. gr. 1·28, for 18 hours on the sand-bath, a perceptible amount of silver was dissolved.

Darkened silver bromide was readily acted on by the same nitric acid; after heating for some hours, complete decomposition of the darkened bromide had taken place. M. M. P. M.

The Action of Sulphuric Acid on Platinum. By A. SCHEURER KESTNER (*Compt. rend.*, lxxxvi, 1082).—In an attempt to manufacture fuming sulphuric acid by heating acid sodium sulphate in an earthern retort, the inside of which was lined with platinum, 100 grams of platinum were dissolved in the production of 100 kilos. of acid, which is at the rate of 1 kilo. per ton. The metal was found to be in the residue of sodium sulphate, in a state in which it was soluble in water. In the ordinary concentrating apparatus the amount of platinum dissolved varies from 1 to 8 grams per ton of acid, containing 94 to 99 per cent. of monohydrated acid. But by employing vessels which expose a comparatively small amount of surface to the action of the acid, the amount of platinum dissolved is reduced to 0·1—0·15 gram per ton for ordinary acid, and to 1—1·5 grams per ton for very strong acid (98—99 per cent.). W. C. W.

A New Compound of Palladium. By H. ST. CLAIRE DEVILLE and H. DEBRAY (*Compt. rend.*, lxxxvii, 926—928).—In order to recover the palladium from some mother-liquors of dipalladamine chloride ($PdCl_4.4NH_3$), they were treated with *aqua regia* in presence of excess of sal ammoniac. Instead of the well-known red double chloride, a very deep-red almost black precipitate was obtained, which closely resembled in appearance and solubility the double chloride of iridium and ammonium.

An examination of the precipitate, and of the conditions under which it was formed, showed that it contained only palladium, and that it could be easily obtained by treating with *aqua regia* the yellow palladamine chloride, $PdCl_2.2NH_3$. Analysis assigned to it the formula $Pd_2Cl_6.4NH_3$, thereby showing it to be an ammonia derivative of an hitherto unknown chloride of palladium, the so-called *sesquichloride*.

The following equation doubtless represents its mode of formation, $2(PdCl_2.2NH_3) + Cl_2 = Pd_2Cl_6.4NH_3$.

The new salt is easily destroyed by heat, breaking up into hydrochloric acid, sal-ammoniac, nitrogen, and metallic palladium. It is also decomposed by boiling water, with energetic evolution of nitrogen, the palladium being reduced to protochloride, of which a portion remains combined with the undecomposed ammonia.

The formation of this salt is theoretically interesting, inasmuch as it shows that, with the exception of platinum, all the metals of this natural group can, under suitable conditions, furnish an intermediate chloride of the formula M_2Cl_6. J. W.

Mineralogical Chemistry.

Chemical Composition of Guanaguatite, or Selenide of Bismuth, from Guanaguato, Mexico. By J. W. MALLET (*Amer. J. Sci.* xv, 294).—This mineral has been examined by Castillo, Fernandez, Rammelsberg, and Frenzel, whose analyses left it doubtful whether sulphur was an essential constituent of the mineral, and whether it contained zinc.

The author has analysed the mineral, and has obtained the following numbers:—

Se.	S.	Bi.	Al_2O_3.	Fe_2O_3.	SiO_2.	H_2O.
31·64	0·61	59·62	2·53	trace	3·47	1·46 = 99·33.

Zinc was not found. It is stated that the gangue is galapectite; if this be the case, the pure guanaguatite must have the composition, Se = 34·33, S = 0·66, Bi = 65·01, which gives the atomic ratio of the selenium to the bismuth as very nearly 2 : 3. The mineral is, therefore, a sesquiselenide of bismuth, with a small portion of the selenium replaced by sulphur. C. W. W.

Note on the Crystallisation of Variscite. By A. H. CHESTER (*Amer. J. Sci.* [3], xv, 207).—The crystals usually occur in complicated groups, sometimes forming clusters of a sheaf form. The more common form is orthorhombic, showing the faces P, $\infty\bar{P}\infty$, $\infty\breve{P}\infty$, and 0P. The face $\infty\bar{P}\infty$ is very small; $\infty\breve{P}\infty$ is about the same size as P, so that the crystals may readily be mistaken for hexagonal prisms. The mineral is possessed of a very high lustre, resembling that of beryl. M. M P. M.

Rhabdophane, a New Mineral. By Lettsom (*Compt. rend.*, lxxxvi, 1028).—A specimen in the Mineralogical Collection, Oxford, labelled *Cornwall blende*, was found on examination to contain neither sulphur nor zinc, but to consist essentially of didymium and erbium phosphates. The name *Rhabdophane* has been given to this very rare mineral.

W. C. W.

Tantalite from Coosa Co., Alabama. By J. Lawrence Smith (*Amer. J. Soc.* [3], xv, 203—204).—The mineral occurs loose at the intersection of a ridge filled with quartz and flint rocks, and a mass of detached blocks of granite, more or less disintegrated. The masses of tantalite are irregular, without crystalline form, more or less rounded, with ready cleavage in one direction. Sp. gr. = 7·305 to 7·401.

*Tantalic acid.	Tungstic acid.	Stannic acid.	Manganese protoxide.	Iron protoxide.	Copper oxide.	
79·65	1·10	0·87	3·72	13·51	0·89	= 99·74

M. M. P. M.

Mother-Liquors of the Brine Springs of Volterra. By A. Funaro (*Gazzetta chimica italiana*, viii, 71—75).—The examination of these mother-liquors was undertaken with a view to ascertain if crude potash salts for manuring vines, cereals, &c., could be obtained from them. The density of the liquid was 1·215, and the analytical results per 1000 grams were as follows:—

Oxide of sodium	124·500
„ potassium	21·616
„ calcium	2·240
„ magnesium	18·015
Ferric oxide	0·200
Sulphuric anhydride	12·174
Chlorine	186·050
Iodine	·012

The amount of iodine varied greatly in different samples. These mother-liquors are at present thrown away, but the author advocates their use as a source of potassium salts. The latter part of the paper is chiefly occupied with commercial details.

C. E. G.

Organic Chemistry.

Regularities in the Boiling Points of the Chlorinated Ethanes. By W. Staedel (*Deut. Chem. Ges. Ber.*, xi, 746—750).—The author is not inclined to favour Naumann's mechanical theory of the conditions influencing the boiling points of liquids. From a study of the boiling points of the chlorinated ethanes, it is shown that a change of CH_3 to CH_2CH_3 corresponds generally to a rise of 20°, CH_3 to CH_2Cl to a rise of 50° to 70°, CH_2Cl to $CHCl_2$ to a rise of 30°, and $CHCl_2$ to CCl_3 to a rise of 15°. M. M. P. M.

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* No formulæ are given in the original paper. The tantalic acid contains a very little niobic acid.

Monochloracetylene. By O. WALLACH and O. BISCHOF (*Deut. Chem. Ges. Ber.*, xi, 751—753).—When the barium or calcium salt of β-dichloracrylic acid is heated with baryta-water, a violent explosion ensues. By conducting the operation in a stream of hydrogen and condensing the resulting gas in bromine, *tetrabromomonochlorethane*, C_2HClBr_4, is obtained: hence the gas evolved by the action of alkalis upon β-acrylic acid is monochloracetylene, C_2HCl,—

$$CCl_2{=}CH.COOH = CCl{\equiv}CH + HCl + CO_2.$$

M. M. P. M.

Action of Sulphuric Acid on Acetylene. By S. ZEISEL (*Liebig's Annalen*, cxci, 366—375).—The author finds that pure acetylene, when treated successively with concentrated sulphuric acid and water, does not yield crotonic aldehyde, as stated by Lagermark and Eltekoff (*Ber.*, x, 687; and this Journal, 1877, ii, 583). The crotonic aldehyde obtained by these chemists he believes to be derived from vinyl bromide or chloride existing as an impurity in the acetylene employed by them. J. R.

Action of Dehydrated Oxalic Acid on Primary, Secondary, and Tertiary Alcohols. By A. CAHOURS and E. DEMARÇAY (*Compt. rend.*, lxxxvi, 991—996).—The authors stated in a previous paper that, by the action of dehydrated oxalic acid on primary alcohols, a large yield of oxalate is obtained, whereas in the case of secondary alcohols only a relatively small quantity of the oxalate is formed. This observation was confirmed by the following experiments:—3 molecules of methyl alcohol and 1 of oxalic acid, heated at 50° for several hours and then distilled, yielded carbon monoxide and dioxide, unchanged methyl alcohol, methyl oxalate, about equal to the weight of oxalic acid originally employed, and a trace of methyl formate.

Primary octyl alcohol from the essential oil of *Heraclium sphondylium*, on treatment with dehydrated oxalic acid, yielded octylene, (b.-p. 120—125°), and octyl formate (b.-p. 195—197°). These substances were formed by the decomposition of the octyl oxalate—

$$(C_8H_{17})_2C_2O_4 = C_8H_{16} + C_8H_{17}.CHO_2 + CO_2.$$

Secondary octyl alcohol (methyl-hexyl carbinol) under similar conditions gave carbon monoxide and dioxide, formic acid, and a small quantity of octyl formate. Trimethyl carbinol and dimethyl-ethyl carbinol are split up by the action of oxalic acid into water and hydrocarbons, viz., butylene and amylene respectively. W. C. W.

On the Formation of Alcohols in Piria's Process for the Preparation of Aldehydes. By S. PAGLIANI (*Gazzetta chimica italiana*, viii, 1—9).—The process originally proposed by Williamson for preparing aldehydes by distilling a mixture of a formate with the salt of an acid of the fatty series, and subsequently carried into effect by

Piria, is very far from yielding the amount of product indicated by the equation—

$$(C_nH_{2n-1}O_2)_2Ca + Ca(CHO_2)_2 = 2C_nH_{2n}O + 2CaCO_3.$$

As is well known, aldehydes readily take up hydrogen to form alcohols, and Dumas and Stas have shown that hydrogen is a product of the destructive distillation of a formate, so that it seemed highly probable that a portion of the aldehyde at the moment of its formation might combine with the nascent hydrogen from the formate, giving rise to the corresponding alcohol. This has been shown to be the case in one instance by Lieben and Paternò, who observed methyl alcohol amongst the products of the destructive distillation of calcic formate.

The formation of butyraldehyde by the distillation of a mixture of a formate and butyrate has been often repeated by different observers, who found that only from 50—54 per cent. of the crude distillate consisted of the aldehyde. This remarkable constancy in the proportion of the aldehyde induced the author to believe that the secondary products would be found to bear a constant relation to the chief product. With this view he undertook the examination of the secondary products: these, after separation of the bulk of the butyraldehyde, were submitted to careful fractional distillation, and the fractions treated with hydrogen-sodium sulphite. In this way some butyraldehyde and butyrone were separated, and also a small quantity of a compound which appeared to be identical with Chancel's butyral. The portion of the liquid which was unacted on by the sulphite, after being washed with sodium carbonate solution and dried by potassium carbonate, was again fractioned, when a liquid boiling at 116° was isolated, identical with normal butyl alcohol, as was shown by its vapour-density, by the boiling point of the chloride (77—78°), and by the products of its oxidation. The quantity of butyl alcohol appeared to be about 11—12 per cent. of the secondary products.

By converting the remaining fractions into benzoic salts by treatment with benzoic acid and hydrochloric acid, the author succeeded in obtaining indications of the existence of secondary heptylic alcohol formed by hydrogenation of butyrone.

The author has also ascertained that ethyl alcohol is formed when a mixture of a formate and an acetate is distilled, but not when an acetate is distilled alone. This shows undoubtedly that the alcohol is formed in these reactions by the union of the aldehyde with the hydrogen derived from the formate, as the salts of the fatty acids higher in the series than formic acid do not yield hydrogen when distilled.

C. E. G.

Action of Sulphurous Anhydride on Alcohols. By S. Pagliani (*Gazzetta chimica italiana*, viii, 101—104).—The alcohols were saturated with pure dry sulphurous anhydride at the ordinary temperature, and then heated at 190—220° in sealed tubes. The product was diluted with water, the oily layer separated and distilled, and the acid liquid saturated with baryta, and the barium salts examined.

Ethyl Alcohol.—After 30 hours' digestion, monoclinic crystals of sulphur were observed in the tube. On adding water to the product, an oily layer separated, consisting of ethyl oxide and mercaptan, whilst the aqueous solution contained sulphuric acid and ethyl-hydrogen sulphate (ethyl-sulphuric acid). In all probability the following reactions take place:—

$$
\begin{aligned}
C_2H_5.OH + SO_2 &= C_2H_5.SO_2.OH.\\
C_2H_5.SO_2.OH + 3SO_2 &= C_2H_5.SH + 3SO_3.\\
3SO_3 + 3C_2H_5.OH &= 3SO_2(OH)OC_2H_5.\\
3SO_2(OH)OC_2H_5 + 3C_2H_5.OH &= 3H_2SO_4 + 3(C_2H_5)_2O.\\
3H_2SO_4 + 3C_2H_5.OH &= 3SO_2(OH)OC_2H_5 + 3H_2O.\\
3SO_2 + 2H_2O &= 2H_2SO_4 + S.
\end{aligned}
$$

Normal Butylic Alcohol.—The product, which was dark-coloured, contained butyl mercaptan, but no oxide could be detected. The aqueous solution gave a crystalline barium salt, although in quantity insufficient for analysis.

Isobutylic Alcohol.—Isobutyl mercaptan and isobutyl hydrogen sulphate were recognised, but no isobutyl oxide.

Fermentation Amyl Alcohol.—No alteration in the optical rotary power of this alcohol could be observed after heating it with sulphurous anhydride for 30 hours at 200°.

No deposition of sulphur was observed with any of these three alcohols.
C. E. G.

On Alcoholic Potash. By E. J. MAUMENÉ (*Compt. rend.*, lxxxvi, 890—892).—Since the author brought forward the idea in *Les Mondes* (1872, 668), that the reducing action of alcoholic potash depended on the formation of a salt of potash, $C_4H_7O_3.KO$, which theory did not receive general acceptation, he has succeeded in obtaining this salt in quantity sufficient to establish its existence.

All alcoholic solutions of potash preserved from air and carbon dioxide deposit after some time a salt consisting of dark-coloured crystalline grains, which may be purified by dissolving them in 15 or 20 times their weight of water, filtering through charcoal, and evaporating. The salt becomes anhydrous at 100°, and gives some characteristic precipitates with certain metallic solutions, such as those of iron, mercury, silver, and platinum.

The following is the author's analysis of the substance dried at 100°:—

1,000 parts left 676·2 $KOCO_2$ (coloured salt).
,, ,, 676·4 ,, (colourless salt).
,, ,, 676·5 ,, (calculated).

The combustion with oxide of copper gave—

	Colourless acid.		Coloured salt.		Calculated for $C_4H_7O_3.KO$.
C....	23·54	23·55	23·49	23·48	23·53
H....	7·03	6·98	7·20	7·11	6·86

The composition, the author therefore concludes, is $C_4H_7O_3.KO$.
J. M. T.

Decomposition of Ethyl Alcohol by Zinc Chloride at High Temperatures. By W. H. GREENE (*Compt. rend.*, lxxxvi, 1140).—

Alcohol was allowed to fall drop by drop upon zinc chloride, heated to a high temperature, the liquid products were condensed, and the gases were absorbed by petroleum, bromine, and water.

The water was found to have absorbed a small quantity of hydrochloric acid; the bromine had absorbed a considerable quantity of ethylene, and the petroleum little or nothing. Hydrogen and ethyl hydride were also formed. The liquid products were ether, water, aldehyde, polymerides of ethylene, and undecomposed alcohol. The aldehyde and ethylene were formed in nearly corresponding quantities, probably according to the equation, $2C_2H_6O = C_2H_4O + C_2H_4 + H_2O + H_2$. The hydrochloric acid produced polymerises some of the aldehyde; it is formed by the action of water on the chloride of zinc.

C. W. W.

New Mode of Formation of Ethyl Oxide. By W. H. GREENE (*Compt. rend.*, lxxxvi, 1141).—In a previous paper (*ibid.*, lxxxvi, 624) the author showed that by the action of sodium monoxide on ethylene bromide, ethylene oxide is produced. In the same way, by heating sodium monoxide at 180°, with ethyl iodide, ethyl oxide is formed in considerable quantity.

Similar experiments with chloro- and bromo-benzene have as yet given no results. C. W. W.

Derivatives of Tetrachlor-ether. By E. PATERNÒ (*Gazzetta chimica italiana*, viii, 182; and *Deut. Chem. Ges. Ber.*, xi, 750—751). —A claim of priority over Busch in the discovery of the compound, $CCl_2{=}CClOC_2H_5$, and the bromine addition-compound of this body. M. M. P. M.

New Method of Preparation of Isopropylglycol. By HANRIOT (*Compt. rend.*, lxxxvi, 1139).—Acetobromhydrin is prepared by the action of acetyl bromide on glycerin, and the product of the reaction is distilled under a pressure of about 10 cm. of mercury. The acetobromhydrin is then hydrogenised by means of Gladstone's copper-zinc couple, freed from zinc by potassium carbonate, and the magma extracted with alcohol. The acetate of isopropylglycol, when saponified by potash, furnishes a product, distilling at 188°, and having all the properties of Wurtz's propylglycol, which is therefore isopropylglycol, $CH_2(OH).CH(OH).CH_3$. C. W. W.

Derivatives of Glycerin. By HANRIOT (*Bull. Soc. Chim.* [2], xxix, 397—400).—In the preparation of monochlorhydrin on the large scale, the author obtained a small quantity of an isomeric substance, boiling at 144—146°. This body was subjected to the action of nascent hydrogen, with the object of converting it into normal propylglycol; but the chief products of the action were polyglycerins, which could not be distilled without decomposition.

The author finds that isopropylglycol may be easily prepared by a process on which he is still engaged. It consists in acting upon dry glycerin with acetyl bromide, and subjecting the acetobromhydrin thereby produced to the action of the copper-zinc couple. J. R.

On an Isomeride of Monochlorhydrin. By HANRIOT (*Compt. rend.*, lxxxvi, 1139).—Theory shows two possible isomerides of the first hydrochloric ether of glycerin, viz., chloropropylglycol,

$$CH_2(OH).CHCl.CH_2(OH),$$

and chlorisopropylglycol, $CH_2(OH).CH(OH).CH_2Cl$. The second of these two bodies was obtained by Berthelot, by the action of hydrochloric acid on glycerin; the first also occurs amongst the products of this reaction, being contained in the higher boiling portions. By fractional distillation it is obtained as a colourless liquid, boiling at 145° under a pressure of 10 mm. of mercury (monochlorhydrin boils at 139° at the same pressure), and having exactly the composition of monochlorhydrin.

This body is probably identical with that which Henry obtained by the action of hypochlorous acid on allylic alcohol; it is, however, difficult to determine its constitution, as it is easily transformed into polyglyceric compounds. C. W. W.

Vitreous Fused Saccharose. By H. MORIN (*Compt. rend.*, lxxxvi, 1083—1085).—When saccharose is heated with water, under certain conditions, and allowed to cool slowly, it forms a vitreous, translucid mass, interspersed with prismatic crystals; but if the fused product is cooled rapidly, it loses its semi-crystalline character, and forms a compound, which contains 3·28 per cent. of water, and has a sp. gr. of 1·966 at 14·5°. If the melted saccharose is plunged into a freezing mixture, it splits up on cooling into a thousand pieces.

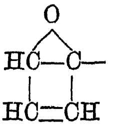
The vitreous saccharose on heating to 100° becomes opaque, and if exposed to a temperature of 130° for several hours, it loses its rotatory power, owing to its conversion into an optically inactive sugar, possessing strong reducing properties. W. C. W.

Nitrosofurfurine and Oxynitrosofurfurine. By R. SCHIFF (*Gazzetta chimica italiana*, viii, 76—80).—Some time since the author described a substance, $C_{30}H_{27}N_5O_{15}$, obtained by the action of a concentrated solution of potassium nitrite on furfurine sulphate (this volume, p. 47), nitrogen being at the same time evolved. He now finds, when very dilute solutions of the potassium and furfurine salts are mixed, that a yellow precipitate is produced, which, after purification by crystallisation from ether, melts at 112°, and has the composition of nitrosofurfurine, $C_{15}H_{11}(NO)N_2O_3$; under these conditions no gas is evolved. Nitrosofurfurine is insoluble in water, moderately soluble in alcohol and in ether, from which it separates in large, golden yellow, triclinic crystals. Furfurine is therefore an imide base, since only one atom of hydrogen can be replaced by an alcohol radicle; the acetyl derivative is only decomposed with difficulty by alkaline solutions; nitrous acid converts it into a nitroso-derivative; and allylthiocarbimide and aldehydes are without action on it.

The author considers that the compound $C_{30}H_{27}N_5O_{15}$, is formed from 1 mol. nitrosofurfurine and 1 mol. furfurine, in the following manner:—

$$C_{15}H_{11}N_3O_4 + C_{15}H_{12}N_2O_3 + 2H_2O + 6O = C_{30}H_{27}N_5O_{15}.$$

The molecule of furfurine contains the group C_4H_3O three times, and as the oxygen in this group does not appear to be hydroxylic or ketonic or aldehydic, he believes it has the constitution—



so that 1 mol. of furfurine + 1 mol. nitrosofurfurine would contain this group six times, and consequently would be capable of taking up six atoms of oxygen, the oxygen united with the two carbon atoms being displaced by two linked oxygen-atoms, —O—O—. Some natural alkaloïds, such as cinchonine and strychnine, when treated with potassium nitrite, are oxidised in a somewhat similar manner, with evolution of nitrogen (Schützenberger, *Compt. rend.*, xlvii, 79).

C. E. G.

On β-Chlorobutyric Acid and some of its Derivatives. By L. BALBIANO (*Gazzetta chimica italiana*, viii, 90—101).—After a summary of the literature of the action of chlorine on butyric acid, the process by which the new chlorobutyric acid was prepared is given. Chlorine is passed into pure fermentation butyric acid, at 90—95°, in sunlight, in quantity sufficient to convert it into the monochlorinated derivative. The gas is rapidly absorbed, and hydrochloric acid is evolved in abundance. As the chlorinated acid is decomposed by distillation, the product is freed from unaltered butyric acid by washing it with successive small quantities of ice cold water as rapidly as possible. It is, however, far from pure.

Ethyl Chlorobutyrate.—The crude product of the action of chlorine on butyric acid is mixed with an equal volume of alcohol, and saturated with hydrochloric acid; after 12 hours it is heated at 100°, to expel hydrochloric acid, then washed, dried, and submitted to fractional distillation. In this way the ethyl salts of butyric acid and monochlorobutyric acid may be isolated. Ethyl monochlorobutyrate, $C_6H_{11}ClO_2$, is a colourless liquid, of agreeable odour, which boils at 168—169°, and remains liquid at −20°. It density at 0° is 1·072. The ethyl salt is soluble in ether and alcohol, insoluble in water, but is decomposed in contact with the latter, with formation of hydrochloric acid.

Oxybutyric Acid.—In order to ascertain the constitution of the chlorobutyric acid, the ethyl salt was decomposed by boiling with baryta solution, when it yielded a well crystallised crotonic acid (m. p. 70·5—71·5°), and a small quantity of a syrupy acid; similar results were obtained by employing a lower temperature, 50—60°, and also when alcoholic potash was used. The syrupy acid yields a crystalline sodium salt, having the composition of sodium oxybutyrate, $C_4H_7O_3$ Na; it is very soluble, both in water and in alcohol, and is deliquescent. The pure free acid obtained by decomposition of the zinc salt with hydrogen sulphide, when dried over sulphuric acid, forms a syrupy liquid, without any trace of crystallisation.

The *silver* salt, $C_4H_7O_3Ag$, crystallises in colourless, slender needles, sparingly soluble in cold water.

The *barium* salt $(C_4H_7O_3)_2Ba$, is uncrystallisable and deliquescent, and very soluble in water and in alcohol.

It has been shown by Hemilian that solid crotonic acid has the structure, $CH_3.CH{=}CH.COOH$, therefore the ethyl chlorobutyrate from which it is derived must be either α, $CH_3.CH_2.CHCl.COOC_2H_5$, or β, $CH_3.CHCl.CH_2.COOC_2H_5$, and the oxybutyric acid has all the properties of β-oxybutyric acid, prepared from acetoacetic ether by hydrogenation,

$$CH_3.CO.CH_2.COOH + H_2 = CH_3.CH(OH).CH_2.COOH,$$

and by Markownikoff, from the cyanide, $CH_3.CH(OH).CH_2.CN$, so that the β-chlorobutyric acid prepared as above described, has the constitution, $CH_3.CHCl.CH_2.COOH$. The author has ascertained that no appreciable quantity of any isomeric monochlorobutyric acid is formed when butyric acid is chlorinated under the conditions mentioned. C. E. G.

Nitroso-Compounds of the Fatty Series. (II.) By V. MEYER and J. ZÜBLIN (*Deut. Chem. Ges. Ber.*, xi, 692—697).—In a previous communication (*Ber.*, xi, 320, and this volume, 487) the authors described the nitroso-ketone produced by the action of nitrous acid on the ethyl ether of methyl-aceto-acetic acid, and pointed out that by apparently insignificant changes in the method of preparation, other bodies were obtained; they now detail the conditions of formation, and the nature of these substances.

Nitroso-methyl acetone, $CH_3.CO.CH(NO).CH_3$, is obtained, as formerly described, by the action of nitrous acid on the ether of methyl-aceto-acetic acid dissolved in an excess (3 molecules) of aqueous potash.

Ethyl α-nitroso-propionate, $CH_3.CH(NO).COOC_2H_5$, results from the action of nitrous acid on methylaceto-acetic ether, when it is dissolved in 1 mol. alcoholic potash, and afterwards decomposed by water. The following will explain its formation:—

$$CH_3.CO.C(NO)(CH_3)(COOC_2H_5) + H_2O = CH_3.COOH + CH(NO)(CH_3)(COOC_2H_5).$$

It crystallises in beautiful long prisms or needles, which melt at 94°, and boil with slight decomposition at 233° (corr.). It has acid properties, due to the group —CH(NO)—. Unlike that of the nitroso-ketone, its alkaline solution is colourless. It does not give any colour reaction with phenol and concentrated sulphuric acid. It dissolves easily in alcohol and ether, &c., and can be recrystallised from hot water. On boiling with dilute aqueous alkali, it is saponified.

α-Nitroso-propionic acid, $CH_3.CH(NO).COOH$, may also be prepared like the ethyl ether, except that the solution, after being treated with nitrous acid and made alkaline, is allowed to stand for several days, then saturated with sulphuric acid, and agitated with ether. The free acid forms small, white, granular crystals, quite different from those of the two preceding bodies. It is neither fusible nor volatile, but decomposes suddenly at 177°, and gives no colour reaction with phenol and sulphuric acid. It dissolves to a colourless solution in alkalis, and decomposes carbonates. It is easily soluble in water and alcohol, but with difficulty in ether.

Silver salt, $CH_3.CH(NO).COOAg$. Is insoluble in water, and but little acted on by light.

The authors have been unable to prepare nitrosobutyric acid, or its ether, in a manner similar to that described above for nitroso-propionic acid, as they have always obtained instead nitroso-ethyl-acetone, $CH_3.CO.CH(NO).CH_2.CH_3$, the formation of which from ethylic ethyl-aceto-acetate they have previously described. It crystallises in white needles (m. p. 54°), which are partially decomposed on distillation at the ordinary pressure; under diminished pressure, however, it distils without decomposition, at 185° (corr.).

Nitroso-acetone, $CH_3.CO.CH_2(NO)$. As already mentioned in their former paper, there is produced from aceto-acetic ether with 1 molecule aqueous potash and nitrous acid, nitroso-acetic ether, whereas if 1 molecule alcoholic potash be used, there results a non-volatile oil, which as yet has not been obtained pure. If, however, several days are allowed to elapse after the addition of alkali, nitroso-dimethyl-ketone is obtained, together with a considerable quantity of an oil, which does not solidify. The following represents the formation of the first body:—$CH_3.CO.CH(NO)(COOC_2H_5) + HO.H = CO_2 + C_2H_5.OH + CH_3.CO.CH_2(NO)$.

Nitroso-acetone consists of silvery plates or prisms (m. p. 65°), which are easily soluble in ether, and in cold or hot water. It passes over readily with steam, but cannot be distilled alone without decomposition, although its next higher homologue can. It has acid properties, and its alkaline solution is intensely yellow; it gives a yellow solution with phenol and sulphuric acid. The statement made in a former communication, that nitroso-compounds give a red coloration on treatment with aniline and acetic acid, is incorrect. The authors are continuing their investigations. T. C.

Candles Altered by Long Exposure to Sea-Water. By J. H. GLADSTONE (*Chem. News*, xxxvii, 165).—The author obtained some candles, which are stated to have been recovered from the wreck of a Dutch vessel sunk in Vigo Bay during the war in 1702, and had been submerged for 173 years. Analysis showed that the fat has been converted in great measure into calcium and sodium stearates, doubtless by the slow replacement of the triatomic group, C_3H_5, in the stearin by 3 atoms of the metal, with simultaneous production of glycerin. Although the calcium in sea-water is far less abundant than the sodium, it appears to have had a much greater effect, but it is of course impossible to say whether the one salt has not been formed by double decomposition of the other. The most interesting point is, that although the fats have been exposed to an unlimited amount of sea-water, and chemical change between them has been possible, the double decomposition has proceeded so extremely slowly that the reaction is only about half completed at the present time. D. B.

Derivatives of Ethylic Isobutylacetyl Acetate. By E. DEMARÇAY (*Compt. rend.*, lxxxvi, 1085—1088).—In the preparation of ethylic mono-bromo-isobutylacetyl-acetate, one portion of the ethereal salt is not acted on by the bromine, whilst another portion is converted into the dibromo-compound. By the action of alcoholic potash on this crude product, several bodies are formed, viz.:

Isobutyl-acetone, $CH_3.CO.CH_2.CH_2.CH(CH_3)_2$ (b. p. 145°), due to the action of alcoholic potash on ethylic isobutylacetyl-acetate.

Heptic acid, $3C_7H_{10}O_2 + H_2O$, and *methyl-isobutyl-glyceric acid*, $COOH.C[CH_2CH(CH_3)_2]OH.CHOH.CH_3$. The formation of these two acids may be represented by the following equations:—

1. $C_{10}H_{17}BrO_3 + 2H_2O = C_2H_6O + HBr + CO_2 + H_4 + C_7H_{10}O_2$.
2. $C_{10}H_{17}BrO_3 + 4H + 4H_2O = 2C_2H_6O + 2HBr + 2C_8H_{16}O_4$.

Oxyheptic acid, $3C_7H_{10}O_3 + H_2O$, and *glycollic acid* are formed in small quantities only if the bromination of the ether has been properly conducted, as they originate from the action of potash on the dibrominated ether.

These results agree with the author's observation that only the mono-substituted ethers of acetyl-acetic acid yield acids belonging to the series, $C_nH_{2n-4}O_2$. W. C. W.

Ethylic Isobutylacetylacetate. By E. DEMARÇAY (*Compt. rend.*, lxxxvi, 1135—113-).—In the previous paper the author described the different reactions which monobrom-isobutylacetylacetic ether undergoes when treated with alcoholic potash; he now gives the methods of preparing the different products of the reactions.

Isobutylacetylacetic ether, mixed with its own weight of ice, is treated with successive small portions of bromine, care being taken that the temperature does not rise above −5°. When all the bromine has been added, the liquid is allowed to get warm, and soon becomes colourless; it is then poured in small portions into excess of strong alcoholic potash.

From the liquid, free from alcohol, hydrochloric acid separates an oil which, when purified and fractionally distilled, yields caproic acid, whilst isobutylmethylglyceric acid remains in the flask.

Caproic acid thus obtained has the properties of the acid described by Kohn (*Annalen*, cxc, 390). The calcium salt, however, crystallises with $3H_2O$, and the barium salt with $2H_2O$, whilst Kohn's salts were anhydrous.

Isobutylmethylglyceric acid is a mobile liquid, which, when heated, is changed into gummy anhydrides, whilst a small portion distils with vapour of water. The barium salt is anhydrous, and crystallises in small needles. The calcium salt is also anhydrous and crystallises in needles, which are more soluble in cold than in hot water.

Heptic, oxyheptic, and glycollic acids can be extracted by ether from the water from which the preceding acids have been distilled, and are separated by crystallisation from water and chloroform, in which heptic acid alone is soluble. Heptic acid forms flat needles, having a satiny lustre, and melting at 151° to a colourless liquid, which boils and decomposes at a higher temperature. It is slightly soluble in cold water, colours ferric chloride pale brown, and decomposes carbonates only on heating. Its composition is represented by the formula, $3C_7H_{10}O_2 + H_2O$, and that of its barium salt by $C_{21}H_{30}BaO_7$; it would seem, therefore, that the acid should have the formula, $C_{21}H_{32}O_7$. A closer study of its reactions shows, however, that it is only in its less energetic reactions that the triple molecule forms a single group, whilst bromine, phosphorus pentachloride, &c., break up this group.

The study of oxyheptic acid confirms this view of the composition of heptic acid. This body is easily formed by the action of alcoholic potash on dibrominated isobutylmethylglyceric ether. After crystallisation from boiling water, it forms pearly scale smelting at 185°, and having the composition $3C_7H_{10}O_3.H_2O$. Pentachloride of phosphorus converts it into a chloride, $C_7H_8OCl_2$, boiling, with decomposition, at 21°.* Ammonia converts this chloride into the corresponding amide, melting and decomposing at 251°. Alcohol converts the chloride into the ether $C_7H_9O_2.OC_2H_5$, boiling at 129—130°, under a pressure of 10 c.m.; at 230—240°, with decomposition, at the ordinary pressure. If ammonia be added to the solution of the chloride in a large quantity of alcohol, an amide is obtained on evaporation, in slender needles, melting at 87°, and having the composition $C_7H_9O_2NH_2$. C. W. W.

Behaviour of Acrylic Acid when fused with Alkalis. By E. ERLENMEYER (*Liebig's Annalen*, cxci, 376—384).—The author maintains the correctness of the statement made by him in a former paper, that acrylic acid, when fused with potash, yields acetic and formic acids. In no instance has he found that acrylic acid is carbonised by melting potash, as is stated by Linnemann to be the case when dry potash is used. J. R.

Normal Methyl-oxybutyric Acid and its Derivatives. By E. DUVILLIER (*Compt. rend.*, lxxxvi, 1026—1028).—When normal ethyl bromobutyrate is added to a solution of sodium methylate in methyl alcohol, a liquid is obtained which boils at 150—155°, and consists of a mixture of the ethyl and methyl ethers of methyl-oxybutyric acid. The methyl ether is produced by the action of methyl alcohol on the ethylic methyl-oxybutyrate. The acid, $CH_3.CH_2.CH(OCH_3).COOH$, was obtained by saponifying the ethers with alcoholic potash, and decomposing the resulting potassium salt with dilute sulphuric acid. It is a slightly oily liquid, soluble in water, alcohol, and ether. Its salts bear a striking resemblance to the ethyl-oxybutyrates; they are all very soluble in water and alcohol, and do not crystallise. W. C. W.

Occurrence of Tricarballylic Acid in Beet-Juice. By. E. O. v. LIPPMANN (*Deut. Chem. Ges. Ber.*, xi, 707—708).—A small quantity of an amorphous granular precipitate was deposited in a vacuum-pan which had been working for about two weeks. This was found to consist, after purification, of the calcium salt of tricarballylic acid, recognised by its properties and by the analysis of the free acid and its silver salt. This body was probably formed by the decomposition of calcium citrate, which sometimes occurs in pans used in the manufacture of sugar from beetroot. The author has, however, not been able to obtain any more of the same body from a similar source.

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* So in the original: perhaps a misprint for 221°.—H. W.

T. C.

Note on Carbamine-sulphacetic Acid (Carbamine-sulphoglycollic Acid). By M. Nencki (*J. pr. Chem.* [2], xvii, 69—70).—This body is the same as the carbamine-thioglycollic acid described by Claesson (*Ber.*, x, 1346—1354; this Journal, 1878, i, 37).—When carefully heated in the dry state up to its melting point, this body gives off vapours which produce coughing, and, according to the author, consist of cyanic acid. The syrup which remains after fusion, and does not crystallise on standing for several days, is sulphoglycollic acid. The author has not observed that crystals of thiocarbamidacetic acid are formed when the syrup is left in contact with water as Claesson states, but he has noticed that on melting carbaminesulphacetic acid in a flask, traces of aqueous vapour have been deposited on the sides of the vessel. Probably, therefore, a small part of the acid is decomposed on strongly heating, according to the equation:—

$$NH_2.CS.CH_2.COOH = CSN.CH_2.COOH + H_2O.$$

The melting point of the acid is 142—143°, whereas Claesson gives it as 132—134°. The name carbamine-sulphacetic acid was intended to express the fact that the carbamine residue is united to the acetic acid by the atom of sulphur.

G. T. A.

Occurrence of Aspartic Acid and Tyrosine in the Young Shoots of the Gourd. By E. Schulze and J. Barbieri (*Deut. Chem. Ges. Ber.*, xi, 710—712).—The authors have previously shown (*Ber.*, x, 199) that glutamic acid can be obtained from the young shoots of the gourd. This body probably occurs therein as the amide, which is most likely produced by the decomposition of the albumin during germination.

They now find that a little aspartic acid (400 grams of dry shoots gave 0·5 gram of aspartate of copper) and tyrosine may be extracted from the same source, as is proved by the reactions of the two substances and by the analysis of the copper salt of the aspartic acid. It is probable that the former, like glutamic acid, occurs as the amide (asparagine).

T. C.

Action of Ethyl Chloride on Benzene in Presence of Aluminium Chloride. By Albright, Morgan, and Woolworth (*Compt. rend.*, lxxxvi, 887—888).—Friedel and Crafts having announced in a communication made to the Academy the formation of homologues of benzene by the action of chlorides, bromides, and iodides of alcoholic radicles upon benzene, the authors examined the matter further with the use of chloride of ethyl in place of the iodide. The process employed by Friedel and Crafts for the preparation of methylic derivatives of benzene has given the authors a series of ethylic products, distilling at different temperatures between 90° and 286°.

They are at present engaged in preparing a considerable quantity of these products, in order to isolate the different ethylic homologues, and have already succeeded in obtaining a *hexethylbenzene.*

This body was isolated from the products boiling between 216° and 219°, by fractional distillation, and by crystallisation from alcohol. It crystallises in monoclinic prisms melting at 123°, and sublimes below its fusing point. It boils at 286°; but this is so near the boiling point of hexamethyl-benzene, that it is not unlikely that less than six atoms of hydrogen in the benzene have been replaced by ethyl. J. M. T.

Physical and Chemical Properties of Wood-Oils from Wood-Tar. By G. THENIUS (*Dingl. poly. J.*, ccxxvii, 578—584).—In the distillation of wood-tar in cast-iron retorts, wood-oils are obtained, the first portions of which are quite colourless. By a further rectification of these wood-oils, the following different fractions may be separated:—100 parts of crude oil give 70 parts of rectified light and heavy oils, 25 parts of black residue, and 5 parts of loss. In order to remove the creosote contained in the oils, the latter were repeatedly treated with caustic soda, washed and redistilled. The light and heavy crude oils which the author employed in his experiments were obtained from wood-tar from black firwood found in Austria. The mixed oils have a density of 1·014; 400 kilos. of the latter were distilled in a cast-iron retort, and the sp. gr. of every 12·5 kilos. of distillate taken. The following figures were obtained:—

1.	Distillate of	light yellow	colour.	Sp. gr.	·897	Every 12·5 kilos.
2.	,,	yellow	,,	,,	·915	
3.	,,	,,	,,	,,	·953	
4.	,,	,,	,,	,,	.966	
5.	,,	,,	,,	,,	·979	
6.	,,	,,	,,	,,	·986	
7.	,,	yellowish-green	,,	,,	·993	Every 25 kilos.
8.	,,	,,	,,	,,	·996	
9.	,,	,,	,,	,,	·999	
10.	,,	,,	,,	,,	1·000	Every 50 kilos.
11.	,,	,,	,,	,,	1·014	
12.	,,	,,	,,	,,	1·025	

The pitch left in the retorts amounts to about 100 kilos., and consists of resinous substances, which have to be investigated more fully. The acetic acid present in distillates 1 to 3 was removed by neutralising with potassium carbonate. The distillates 1 to 12 were then treated with 15 per cent. soda-lye, and the separated oil was distilled, the sp. gr. of every 15 kilos. of distillate being ascertained.

1.	Distillate,	colourless.	Sp. gr.	·853
2.	,,	yellowish	,,	·915
3.	,,	,,	,,	·953
4.	,,	,,	,,	·966
5.	,,	greenish-yellow	,,	·988
6.	,,	,,	,,	1·014
7.	,,	,,	,,	1·020
8.	,,	,,	,,	1·025

In this case 40 per cent. of pitch remained as residue in the retort. The distillates 1 to 4 were again treated with 15 per cent. of caustic soda, in order to remove the creosote present. The oil was then shaken up with 2 per cent. of concentrated sulphuric acid, allowed to settle, washed, and completely neutralised with caustic soda. By rectifying the oil in glass retorts on a sand-bath, the following densities were found:—

1.	Distillate, colourless ..		·820
2.	„	„ ..	·828
3.	„	„ ..	·833
4.	Distillate, yellowish..		·838
5.	„	„ ..	·843

These 5 distillates were again treated with 8 per cent. caustic potash to completely remove all creosote; they were then agitated with 5 per cent. of concentrated sulphuric acid, washed with water, neutralised, and subjected to five rectifications. The following boiling points and densities were obtained:—

1.	Distillate,	colourless,	coming over	between	47°	and	52°.	Sp. gr.	·660
2.	„	„	„	„	52	„	57	„	·700
3.	„	„	„	„	57	„	60	„	·750
4.	„	„	„	„	60	„	70	„	·800
5.	„	„	„	„	70	„	80	„	·850

By treating the greenish-yellow distillates (5—8) in a similar manner, the following figures were obtained:—

1.	Distillate,	colourless,	coming over	between	80°	and	90°.	Sp. gr.	·902
2.	„	„	„	„	90	„	100	„	·935
3.	„	yellowish			100		120		·950
4.	„	„			120		140		·965
5.	„	„			140		150		·975
6.	„	greenish			160		185		·985

The following are the most important properties of the first five distillates:—

	1. Distillate.	2. Distillate.	3. Distillate.	4. Distillate.	5. Distillate.
Sp. gr.	0·660	0·700	0·750	0·800	0·850
B. p.	47° to 52°	52° to 57°	57° to 60°	66° to 70°	70° to 80°
Colour	Colourless.	Colourless.	Colourless.	Colourless.	—
Smell	Aromatic; ethereal, like chloroform.	Similar to fine oil of turpentine.	Very slight.	Very little.	Very little, like benzene.
Volatilisation	As volatile as ether.	Not as volatile as the former.	Volatilises without residue.	Volatilises very slowly.	As volatile as Distillate 4.
Burns in a capsule	With bluish white flame.	With blue flame.	With brilliant white colour.	With white flame.	—
Taste	Pungent.	Very pungent.	Mild and aromatic.	Similar to that of oil of coriander.	Pungent.
Solubility	Soluble in alcohol, benzene, and all ethereal oils.	In water, alcohol, benzene, ethereal oils, creosote.	Soluble in strong alcohol, ether, benzene, petroleum.	Soluble in alcohol, ether, benzene, and oil of turpentine.	Soluble in absolute alcohol, ether, benzene, &c.
The oil dissolves	Paraffin, naphthalene, sulphur, &c.	Paraffin, naphthalene, wax.	Paraffin, wax, naphthalene when warmed.	Paraffin, wax, and naphthalene, if heated.	Resins, wax, paraffin, &c., when warmed.
Concentrated sulphuric acid	Red coloration.	Red liquid.	Red liquid.	Red colour.	—
Pure nitric acid	Forms nitro-compounds.	Nitro-compound, heavier than water.	Nitro-compound, heavier than water.	Nitro-compound.	Fuming nitric acid forms a nitro-compound.
Phosphoric acid	No change.	—	—	—	—
Acetic acid	No change.	—	—	—	—
Sulphuretted hydrogen	No change.	—	—	—	—
Ammonium sulphide	No change.	—	—	—	—
Caustic alkalis	Slight turbidity.	—	—	—	—
Calcium chloride	No change.	—	—	—	—
Argentic nitrate	Silver mirror.	—	—	—	—
Chlorine	Formation of a new oily body.	—	Formation of a new oily body.	Oily body, which deposits crystals.	Oily body, depositing crystals.
Refracts the light	Very strongly.	Slightly.	Not at all.	Not at all.	Not at all.

The author gives the following names to these five distillates:—Tridol, Citriol, Rubidol, Coridol, and Benzidol. The next body to benzidol in this series would be benzene; then toluene, xylene, cumene, and cymene. In conclusion, the author mentions that the nitro-compounds give bodies similar to aniline, by reduction with iron filings and acetic acid. These bodies also give colouring matters.

D. B.

Compounds of Organic Bases with Mercuric Chloride. By O. KLEIN (*Deut. Chem. Ges. Ber.*, xi, 743—744).—The object of the author's experiments was to determine to what extent the basic character of the bodies which form compounds with mercuric chloride might be diminished without destroying their power of forming such compounds.

Ortho- and para-toluidine, diphenylamine, dimethylaniline, and naphthylamine readily form crystalline compounds with mercuric chloride, but acetanilide under similar conditions forms no compound.

M. M. P. M.

Formation of Naphthalene and Methyl-violet. By H. BRUNNER and R. BRANDENBURG (*Deut. Chem. Ges. Ber.*, xi, 697—701).—When a mixture of equal molecular weights of dimethylaniline and bromine is heated for some hours at a temperature below 120°, a beautiful blue-violet colouring matter is produced, the analysis of which showed that it had the following composition—

$$C_{20}H_{14}Br(CH_3)_4N_3.3HBr.$$

In the preparation of this body great care is needed, for if the operation goes on too quickly, the temperature rises above 120°, and several red brominated substances are obtained.

Naphthalene and aniline are produced simultaneously with the blue-violet in the above reaction, thus:—

$$2C_6H_5N(CH_3)_2 + Br_4 = C_{10}H_8 + C_6H_5NH_2 + NH_3 + 4HBr.$$

Terrisse likewise obtained naphthalene by the action of Br on a mixture of dimethylaniline and benzylchloride. The authors find that naphthalene is also produced when hydrobromic acid acts on monobromodimethylaniline at 180°, and they consider that an action takes place similar to that which occurs when mesitylene is prepared from acetone and sulphuric acid, the bromine playing the same part as the oxygen-atom in acetone.

Monobromodimethylaniline undergoes no change at 150°, but at 180° it is converted almost entirely into two colouring matters, one a blue, apparently identical with that already described, and the other a red.

T. C.

Derivatives of Phenylenediamines. By E. WUNDT (*Deut. Chem. Ges. Ber.*, xi, 826—830).—*Methenyl-orthophenylenediamine*, $C_6H_4(NH.CH{=}N)''$ is obtained by heating orthophenylenediamine with formic acid for four hours in a flask connected with an upright condenser. It is a white crystalline body, which melts at 167° and boils at about 360°. It is soluble in alcohol, water and acids, and is precipitated from acid solutions on the addition of ammonia. The chloride crystallises with one molecule of water, and forms double salts with gold and platinum chlorides. Para- and meta-phenylenediamines do not form compounds analogous to methenyl-orthophenylenediamine. The para-phenylenediamine formo-compound is deposited from a hot saturated formic acid solution on cooling, in pale violet crystals, which melt at 203·5—204°, and have the composition, $C_6H_4(NHCOH)_2$.

Propenyl-phenylenediamine, $C_6H_4(NH.C_3H_5{=}N)''$, prepared by heating propionic acid with orthophenylenediamine, melts at 168·5—169°, and boils above 360°. It is very soluble in alcohol, ether, and acids, and is deposited from its aqueous solution in thin plates. All the salts of this base, except the picrate, are very soluble in cold water. The picrate is deposited from a hot saturated aqueous solution on cooling in yellow needles, having the composition—

$$C_6H_4N_2H.C_3H_5.C_6H_2(NO_2)_3.OH.$$

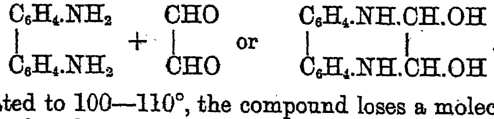
W. C. W.

Aldehyde Derivatives of Amines and Carbamides. By H. Schiff (*Deut. Chem. Ges. Ber.*, xi, 830—835).—From an alcoholic solution of glyoxal and aniline, a substance resembling turpentine separates out, which, after repeated washing with very dilute acetic acid, solidifies to a crystalline mass. The formation of this compound may be represented by the following equation: $4C_6H_7N + 2C_2H_2O_2 = 4H_2O + C_{28}H_{24}N_4$.

Two nitro-compounds, $C_{28}H_{20}(NO_2)_4N_4$ and $C_{28}H_{16}(NO_2)_8N_4$, can be obtained by acting on the crystals with nitric acid and nitrosulphuric acid, at the ordinary temperature.

Glyoxal and Metatoluylenediamine.—The alcoholic solution of the components deposits a brown crystalline mass, having the composition, $2C_7H_{10}N_2 + 2C_2H_2O_2 - 3H_2O$. This substance does not form a double salt with platinum chloride, but on treatment with nitric acid it yields an explosive nitro-compound.

Glyoxal and Benzidine.—The addition of a slight excess of glyoxal to a dilute alcoholic solution of benzidine, produces a finely divided yellow precipitate, which is but slightly soluble in the ordinary solvents. It dissolves however in strong sulphuric acid with an indigo-blue coloration, which is destroyed by the addition of alcohol or water. This glyoxal derivative of benzidine differs from the preceding compounds, as no water is eliminated in its formation. Its composition is probably—



$$\begin{array}{l} C_6H_4.NH_2 \\ | \\ C_6H_4.NH_2 \end{array} + \begin{array}{l} CHO \\ | \\ CHO \end{array} \text{ or } \begin{array}{l} C_6H_4.NH.CH.OH \\ |\qquad\qquad\ \ | \\ C_6H_4.NH.CH.OH \end{array}.$$

When heated to 100—110°, the compound loses a molecule of water and becomes of a chrome-yellow colour.

One molecule of benzidine unites with two molecules of acetaldehyde, valeraldehyde, œnanthol, furfurol, benzaldehyde and salicylaldehyde. The œnanthol compound melts at 113—115°, and is readily soluble in benzene and in ether. The furfurol derivative crystallises well from an alcoholic solution, but the derivatives of the aromatic aldehydes are best crystallised from benzene. The benzoyl compound melts at 231—232°, and on cooling solidifies to a crystalline mass.

A trace of fuming nitric acid produces in a solution of these bodies in cold strong sulphuric acid an intense coloration, which disappears on the addition of water. The acetaldehyde derivative is the only one which forms a double salt with platinum chloride, viz.:

$$2[C_{12}H_8N_2(C_2H_4)_2HCl].PtCl_4.$$

Hydrochloric acid produces an intense red coloration in an alcoholic solution of the furfurol compound. The hydrochloride crystallises in small needles having a metallic lustre; its solution is decomposed by continued boiling.

Benzidine and phthalic anhydride, when heated at 110°, form a crystalline compound, which is partially decomposed by distillation, but can be purified by crystallisation from boiling petroleum.

Benzidine and urea combine at 110—120°, with evolution of ammonia, to form a crystalline compound ($C_{12}H_8.N_2H_4 + 2CON_2H_4 - 2NH_3$), which is insoluble in the usual solvents, but can be purified by dissolving it in strong sulphuric acid, and precipitating by the addition of water.

Benzidine and allylthiocarbimide dissolved in alcohol readily combine to form a compound which is deposited from a hot alcoholic solution in long glistening needles.

Thiocarbamide and œnanthol.—In alcoholic solution no action takes place until a few drops of hydrochloric acid have been added, and the mixture has been warmed, when *œnanthodisulphureide* is formed, which is converted into *heptylenethiocarbimide* on the addition of more hydrochloric acid, $C_7H_{14}(CSN_2H_3)_2 + 2HCl = C_7H_{14}(NCS)_2 + 2NH_4Cl$.

This thiocarbimide is a thick oily liquid possessing a most repulsive odour. It is converted into the disulphureide by the action of alcoholic ammonia.

Aldehydes have no action on ethyl allophanate, biuret, or acetyl carbamide, but with guanidine they form resinous products, which could not be obtained in the crystalline state.

Ethyl allophanate and aldehyde ammonia, when heated to 170°, yield oxyaldin, ammonium carbonate, urethane, and biuret.

The vegetable alkaloïds do not form aldehyde derivatives.

W. C. W.

Remarks on Schiff's Paper "On the Aldehyde Derivatives of Amines and Carbamides." By A. LADENBURG (*Deut. Chem. Ges. Ber.*, xi, 835).—The author disputes Schiff's claim to priority (*Ber.*, xi, 830) in the discovery of the aldehydines. W. C. W.

Acid Imidochlorides and Amidines. By O. WALLACH and A. GOSSMANN (*Deut. Chem. Ges. Ber.*, xi, 753—755).—Benzoyl benzenesulphamide prepared by heating a mixture of benzenesulphamide, $C_6H_5.SO_2NH_2$, and benzoyl chloride, was decomposed by phosphorus pentachloride, whereby the imidochloride was obtained—

$$C_6H_5.CO.NHSO_2.C_6H_5 + PCl_5 = C_6H_5.ClC{=}N(SO_2.C_6H_5) + POCl_3 + HCl.$$

By the action of aniline upon this chloride the amidine,

$$C_6H_5.(NH.C_6H_5)C{=}N(SO_2C_6H_5),$$

was obtained in well defined crystals melting at 131—139°.

This amidine when distilled *per se* yields, besides bodies containing sulphur, benzonitrile, sulphurous acid, and *diphenylamine*.

M. M. P. M.

Direct Union of Oxygen and Sulphur with Benzene and Toluene. By C. FRIEDEL and J. M. CRAFTS (*Compt. rend.*, lxxxvi, 884—887).—The authors first allude to different synthetical reactions brought forward by them at different times depending upon the employment of metallic chlorides, more particularly aluminium chloride, by means of which the replacement of one or more hydrogen atoms may be effected.

They have explained the reaction by supposing that the aluminium chloride reacts on the hydrocarbon, benzene for example, giving hydrochloric acid and an organo-metallic body, $C_6H_5Al_2Cl_5$, containing the residues of both molecules. It is upon this last body that the different chlorine compounds may be made to react, with formation of complex hydrocarbons, acetones, &c., with reproduction of the aluminium chloride. Considering that zinc-ethyl combines directly with oxygen, forming ethylates, it seemed probable that aluminium-ethyl and aluminium organo-metallic compounds generally would behave in a similar manner. They determined therefore to study the action of dry or moist oxygen and air on benzene and toluene in presence of aluminium chloride. Their experiments show that phenol is produced by the action of oxygen on benzene under these circumstances.

This result may be easily understood if we admit the production of the organo-metallic compound already alluded to. This combined with oxygen to form a phenate of aluminium pentachloride, which is decomposed by water with liberation of phenol, thus—

$$C_6H_5,Al_2Cl_5 + O = C_6H_5O,Al_2Cl_5,$$
$$C_6H_5OAl_2Cl_5 + H_2O = C_6H_5OH + (OH)Al_2Cl_5.$$

Toluene behaves in the same manner as benzene, giving a liquid which boils at 200°, and has the composition $C_6H_4CH_3OH$, evidently cresol.

The fixation of oxygen under these conditions led the authors to try the effect of sulphur, and they have found that at 75—80° it reacts easily on benzene in presence of the chloride, forming several sulphur-derivatives of benzene. The first is phenylic mercaptan, C_6H_5HS, formed by a reaction similar to that which gives rise to phenol; it boils at 170—173°, and gives with mercury dichloride a crystalline compound; treated with iodine it yields a crystalline mass of phenyl bisulphide. Phenyl sulphide $(C_6H_5)_2S$, boiling at 288°, is produced at the same time, together with a crystalline substance having all the properties of the compound discovered by Stenhouse, and subsequently examined by Graebe, who assigned to it the formula, $(C_6H_4)_2S_2$, and the name diphenylene disulphide.

J. M. T.

Aurin. By R. S. Dale and C. Schorlemmer (*Deut. Chem. Ges. Ber.*, xi, 708—710).—In a former communication the authors have shown that rosaniline is obtained by heating aurin for a long time with ammonia. Their formula, $C_{20}H_{14}O_3$, for aurin, however, could not be made to agree with Hofmann's formula for rosaniline, $C_{20}H_{18}N_3$. They have, therefore, prepared a much larger quantity of pure aurin, and determined its composition more accurately.

Aurin was obtained in the pure state and in much larger quantity than when phenol is used, from a good commercial aurin, by treating the latter with alcoholic ammonia; the crystalline mass which separated was washed with ammonia and decomposed by acetic acid; the aurin thus obtained was recrystallised from hot alcohol until its composition remained constant.

As the solubility of aurin diminishes with the removal of impurities, the authors have likewise purified commercial aurin by washing with cold alcohol until a relatively small crystalline residue remained, which was then recrystallised several times from alcohol. The analysis of the products obtained by both of the above methods, as well as of aurin from pure phenol, gave concordant results agreeing with the formula, $C_{19}H_{14}O_3$, the percentage of carbon being smaller than in earlier analyses. This bears out the results obtained by Fischer, who has shown that rosaniline prepared from para-toluidine, has the formula and constitution, $C_{19}H_{11}(NH_2)_3$. Aurin is, therefore, $C_{19}H_{11}(OH)_3$. This view is likewise confirmed by the fact that aurin when heated with acetyl chloride gives a tri-acetyl-aurin.

The authors are continuing their investigation. T. C.

Ketones of the Aromatic Series. By W. Staedel (*Deut. Chem. Ges. Ber.*, xi, 744—746).—I. *Derivatives of Benzophenone and Diphenylmethane*, by H. Prätorius. *Diamidobenzophenone*, $C_{13}H_8(NH_2)_2O$, was obtained by Chancel and Laurent by reducing dinitrobenzophenone with ammonium sulphide, and was described by them under the name of *flavin*. This compound is more readily prepared by substituting tin and hydrochloric acid for ammonium sulphide: it crystallises from hot water in slender yellow needles melting at 165°: the chlorhydrate forms small tables, the stannosochloride—

$$C_{13}H_8(NH_2)_2O.2HCl.2SnCl_2,$$

crystallises in plates, and the aceto-compound, $C_{13}H_8(NHC_2H_3O)_2O$, in colourless needles melting at 226·5°.

Diphenylmethane, when heated with nitric acid of 1·4 and 1·5 sp. gr., yields Doer's dinitrodiphenylmethane, which is converted into dinitrobenzophenone (m. p. 189°) on oxidation. Small quantities of a second dinitrodiphenylmethane were obtained, crystallising from benzene in prisms, melting at 118°, and yielding, on oxidation with chromic anhydride, a dinitrobenzophenone which melted above 196°.

Linnemann's dinitrobenzophenone melting at 129°, could not be obtained from the product of the action of nitric acid upon diphenylmethane.

II. *Dioxydiphenyl Ketone.* By F. Gail.

The benzoyl ether of this body, $CO{=}(C_6H_4.O.C_7H_5O)_2$, which was obtained by oxidising the corresponding ether of dioxydiphenylmethane with chromic anhydride, forms brilliant white plates, melting at 181—182°, readily soluble in acetic acid and benzene, and slightly soluble in ether and alcohol.

By decomposing this ether with alcoholic potash, *dioxydiphenylketone*, $CO{=}(C_6H_4OH)_2$, was itself obtained in crystalline plates or needles, probably belonging to the monoclinic system, melting at 210°, soluble in hot water, alcohol, ether, acetic acid, and sodium carbonate.

The ethyl ether of dioxydiphenyl ketone is obtained by the action of alcoholic potash and ethyl iodide on the ketone: a second compound, which is probably the acid ethyl ether, is simultaneously produced.

M. M. P. M.

Fittica's Oxyparatoluic Acid. By E. v. GERICHTEN and W. RÖSSLER (*Deut. Chem. Ges. Ber.*, xi, 705—707).—Although but two oxyparatoluic acids are theoretically possible, yet three have up to the present been described, viz., one (m. p. 184°) by Fittica (*Ber.*, vii, 927), from ordinary nitrotoluic acid (m. p. 190°) from cymene; the second (m. p. 174°) by Jacobsen (*Ber.*, xi, 311), obtained by fusing together paraxylenol and potassic hydrate; the third (m. p. 203) by Flesch, from sulphotoluic acid, and by Gerichten, from chloro- and bromo-toluic acids. From a comparison of the barium and calcium salts of chloro-, bromo-, and nitro-toluic acids (m. p. 190°), the authors have been led to doubt Fittica's results, and to repeat his experiments. They were, however, unable to obtain an oxytoluic acid at all by his method, and found that the acid described by him is not oxyparatoluic, but a nitroxytoluic acid (m. p. 187°). They have succeeded, however, in preparing the oxytoluic acid corresponding with nitrotoluic acid (m. p. 190°), by the action of nitrous acid on the sulphate of amidotoluic acid (from the above nitro-acid), made up to a pulp with water. It melts at 203°, and is identical with Flesch's oxyparatoluic acid, so that the nitro-group stands to the methyl in the ortho-position. There are, therefore, only two, and not three oxyparatoluic acids.

T. C.

Researches on the Nature of the Tannin of Gall-nuts, and on a Crystalline Substance formed by the Action of Arsenic Acid on Gallic Acid. By P. FREDA (*Gazzetta chimica italiana*, viii, 9—16).—The author found that neither a solution of tannin slightly acidulated with acetic acid, nor one of tannin which had been saturated with potassium hydrate and then slightly acidulated with acetic acid, underwent fermentation in contact with yeast, whilst similar solutions of tannin to which glucose had been added, readily fermented. That there was actually glucose present in the tannin employed was proved by decomposing it by boiling with dilute sulphuric acid, neutralising with marble, and adding yeast to the clear solution, when an active fermentation was set up. For the sake of comparison, solutions of salicin and amygdalin were treated in precisely the same way as the tannin solutions, and with the same results. The author infers from this that natural tannin is a glucoside, and not merely a mixture of tannic acid and glucose, or the latter would have fermented in contact with the yeast as the added glucose did.

In preparing digallic acid from gallic acid, by Schiff's method of boiling it in alcoholic solution with arsenic acid, the author obtained a substance crystallising in minute rhomboïdal plates, differing totally from Schiff's amorphous digallic acid. This substance was obtained from the alcoholic solution, after separation of the arsenic by sulphuretted hydrogen and evaporation of the alcohol, by dissolving the residue in a small quantity of alcohol, adding ether, filtering, and allowing the solution to evaporate. The apparently amorphous substance when examined under the microscope was found to contain minute needle-shaped crystals, which were resolved into rhomboïdal plates on being moistened with water. This substance is exceedingly soluble in water, and the solution has an acid reaction. It is also soluble in ether and in alcohol, but insoluble in benzene. It melts at 210°. Its aqueous solution gives a blue-black precipitate with ferric salts, and is also precipitated by gelatin. C. E. G.

Formation of Digallic Acid, and on the Nature of Tannin. By H. SCHIFF (*Gazzetta chimica italiana*, viii, 87—89).—This is a criticism on the preceding paper. The author says he received two specimens from Freda, presumably the new crystalline substance described by the latter. One of these contained a large quantity of arsenic; the other was found to be a mixture of arsenic acid, digallic acid, gallic acid, ethyl gallate, ellagic acid, arsenic sulphide, pyrogallol, and a volatile organic sulphur compound.

With regard to the glucoside nature of tannin, Schiff is of opinion that not one of the experiments cited gives any indication of the nature of tannin, and still considers the unaltered tannin contained in gall-nuts to be a digallic glucoside, which is very readily decomposible. C. E. G.

Aniluvitonic Acid. By C. BÖTTINGER (*Liebig's Annalen*, cxci, 321—330).—This name is given by the author to a body formed by the spontaneous decomposition of anilpyruvic acid (*ibid.*, clxxxviii, 336), in which aniline and carbon dioxide are simultaneously eliminated. The same product may be obtained directly by boiling a mixture of pyruvic acid and aniline with water. It crystallises in brilliant laminæ, agreeing in composition with the formula $C_{20}H_{18}N_2O_4$. It dissolves in baryta-water, forming the salt $C_{20}H_{18}BaN_2O_5$, which crystallises in needles. The silver salt, $C_{20}H_{16}Ag_2N_2O_4$, is a white crystalline powder, easily soluble in ammonia and nitric acid. The acid combines with hydrochloric acid to form a compound crystallising in long colourless needles of the formula $C_{20}H_{20}N_2O_5.2HCl$. The latter combines with platinic chloride to form a crystalline compound agreeing approximately in composition with the formula—

$$C_{20}H_{20}N_2O_5.2HCl.PtCl_4.$$

Aniluvitonic acid is easily reduced by zinc and hydrochloric acid, yielding aniline and the hydrochloride of a peculiar body not yet examined. J. R.

Preliminary Note on Amyl Hippurate. By G. CAMPANI (*Gazzetta chimica italiana*, viii, 57—59).—The author endeavoured to prepare this ethereal salt by passing hydrochloric acid into an amyl alcohol solution of hippuric acid, but the yield was very small. A far better process is to heat amyl iodide with argentic hippurate and amyl alcohol at about 160° for four hours. The product is heated on the water-bath to remove the amyl alcohol, washed with sodium carbonate solution, and dried. The fluorescent liquid thus obtained, on standing for some months at a low temperature, solidified to a mass of minute needles, which were freed from adhering liquid by pressure. Amyl hippurate, $C_6H_5.CO.NH.CH_2.COOC_5H_{11}$, melts at 28°, and is very soluble in alcohol and ether. It has a feeble fruity odour. It is easily saponified by aqueous solutions of the alkalis.

The author states that the melting point of hippuric acid is 188·5°, and not 187·5° (Conrad). It dissolves in 50 times its weight of amyl alcohol at 9°, and in three parts of the boiling alcohol. C. E. G.

Urethane-benzoic Acid. By C. WACHENDORFF (*Deut. Chem. Ges. Ber.*, xi, 701—705).—Urethane-benzoic acid, prepared according to Griess's method (*Ber.*, ix, 796), by the action of nitrous acid on oxethylcarbimidamidobenzoic acid, when heated a few degrees above its melting point, splits up into carbonic anhydride, alcohol, carboxamidobenzoic acid, and the ethyl salt of urethane-benzoic acid.

The carboxamidobenzoic acid, $CO(NH.C_6H_4.CO_2H)_2$, was isolated by conversion into its ether (m. p. 160°) and recrystallisation from hot dilute alcohol. This ether is identical with that obtained by Griess (*Zeit. f. Ch.*, iv, 389, 650), from uramido-benzoic acid.

Ethyl-urethane Benzoate, $C_2H_5O.CO.NH.C_6H_4.COOC_2H_5$, crystallises from hot dilute alcohol in brilliant plates (m. p. 101°). It is easily soluble in alcohol, benzene, acetic acid, and chloroform; insoluble in cold, but moderately soluble in hot water. It is more stable than the free acid, for it decomposes only partially on distillation; the decomposition is, however, the same as in the case of the acid, except that a resinous substance is produced in addition. A small quantity of a crystalline body (m. p. 160°) was obtained from this, probably identical with the ether of carboxamidobenzoic acid.

The following represents the above decomposition of urethane-benzoic acid:—

$$(1)\ C_2H_5O.CO.NH.C_6H_4.COOH = CON.C_6H_4.COOH + C_2H_6O.$$

$$(2)\ C_2H_5O.CO.NH.C_6H_4.COOH + C_2H_6O = C_2H_5O.CO.NH.C_6H_4.COOC_2H_5 + H_2O.$$

$$(3)\ C_2H_5O.CO.NH.C_6H_4.COOH + H_2O = NH_2.C_6H_4.COOH + C_2H_6O + CO_2.$$

$$(4)\ CON.C_6H_4.CO_2H + NH_2.C_6H_4.COOH = CO(NH.C_6H_4.COOH)_2.$$

Urethane-benzoic acid or its ether, when heated at 180° with alcoholic ammonia, yields urea and amido-benzoic acid (m. p. 172°) or its ethyl salt respectively.

By aqueous ammonia, urethane-benzoic acid is likewise converted into amido-benzoic acid and urea, or its products of decomposition, carbonic acid and ammonia; whilst the ether (the temperature not rising above 100°) in part saponifies and in part yields *urethane-benzamide*, $C_2H_5O.CO.NH.C_6H_4.CO.NH_2$, the constitution of which was proved by its conversion into urethane-benzoic acid. It possesses feeble basic properties, and dissolves in strong hydrochloric acid, especially on warming. It is easily soluble in alcohol, acetic acid, and chloroform, but difficultly soluble even in hot benzene, from which it crystallises in flat needles (m. p. 157°). It is little soluble in cold water, but more easily in hot.

The action of aniline on urethane-benzoic ether is similar to that of ammonia, diphenyl urea being obtained instead of urea.

T. C.

Hydroquinone-Phthaleïn. By A. G. EKSTRAND (*Deut. Chem. Ges. Ber.*, xi, 713—717).—This is a continuation of Grimm's work on the same subject (*Ber.*, vi, 506). Grimm proposed for this body the formula $C_6H_4(CO.C_6H_3.OH)_2O$; it is therefore isomeric with fluoresceïn, but behaves like the phthaleïn of phenol, in this respect corresponding completely with the phthaleïn of orcin. Like the latter it gives a diacetyl and a penta-bromo derivative.

It is obtained by heating 2 mols. hydroquinone and 1 mol. phthalic anhydride with 13 times their weight of zinc chloride, for 14 hours at 120—130°.

The author finds that the yield is three times as great (70 per cent.) when zinc chloride is used instead of sulphuric acid.

Hydroquinone-phthaleïn crystallises in needles (m. p. 226° uncorr.; Grimm gave its m. p. as 233°), and dissolves but sparingly in hot water, separating out on cooling in small tables. It is easily soluble in wood-spirit, alcohol, acetic acid, and acetone. It also dissolves in ether, from which it separates in long needles on evaporation. It is but little soluble even in hot chloroform or benzene, and not at all in light petroleum. The needles which separate out from the alcoholic solution contain, as Grimm showed, 1 mol. alcohol; if, however, the alcoholic solution is diluted with much water, needles are precipitated, which on boiling are converted into thin plates containing 1 mol. of water instead of alcohol (likewise confirming Grimm's results). From the ease with which the alcohol and water replace one another, it is probable that the latter is present as water of crystallisation, and does not go to the formation of hydroxyl-groups so as to give a tetrahydrate; this is confirmed by the fact that this water is driven off below 160°, whilst there is no difference in the properties of the hydrated and dried products; neither has it been possible to obtain a tetra-acetyl-phthaleïn. By alkalis, a solution of the phthaleïn is coloured deep violet, which on boiling or standing becomes brown and muddy. In sulphuric or hydrochloric acids it dissolves to a red liquid, and the latter acid gives a crystalline compound, corresponding probably with the hydrochloride of orcin-phthaleïn, but it has not yet been investigated.

Diacetyl-phthaleïn, $C_{20}H_{10}O_5(C_2H_3O)_2$, obtained by heating the phthaleïn with acetic anhydride for two or three hours, forms colourless crystals (m. p. 210° uncorr.).

Bromo-compound.—When a solution of the phthaleïn in alcohol or acetic acid is acted on by bromine, the mixture allowed to stand, and then diluted with water, a yellow flocculent precipitate is obtained, soluble in dilute alcohol, but it has not yet been possible to get it in a crystalline form.

Pentabromo-phthaleïn, $C_{20}H_7Br_5O_5$, is obtained as a yellow crystalline precipitate when an excess of bromine is added to an acetic acid solution of the phthaleïn, and the mixture boiled for a long time. The pure compound is a colourless crystalline powder (m.p. over 300°), insoluble in acetic acid, but easily soluble in nitrobenzene, from which it separates in small tables. It gives a colourless solution with alkalis.

Phthalin, $C_{20}H_{14}O_5$, is obtained when phthaleïn is heated for four hours with zinc dust and soda solution. It crystallises from benzene in large colourless tables (m.p. 202° uncorr.), containing 1 mol. benzene; it dissolves to a colourless solution in alkalis, and to a red liquid in sulphuric acid, which on dilution with water gives an olive-green flocculent precipitate of the phthalidin; this latter dissolves in ether with a green fluorescence; the ethereal solution, however, soon oxidises, with the production of a dark violet powder. Phthalin gives no compound with hydrochloric acid.

Diacetylphthalin, $C_{20}H_{12}O_5(C_2H_3O)_2$, is obtained by boiling the phthalin for two hours with an excess of acetic anhydride. It crystallises in colourless prisms (m. p. 190° uncorr.), and dissolves in wood-spirit much more easily than diacetylphthaleïn. At first it is not acted on by alkalis, but on gentle warming gives a violet coloration.

T. C.

Chloro-Derivatives of Naphthalene. By E. FISCHER (*Deut. Chem. Ges. Ber.*, xi, 735—741).—By treating an intimate mixture of naphthalene and potassium chlorate with hydrochloric acid, naphthalene dichloride and tetrachloride were obtained as the main products of the reaction. Laurent's β-naphthalene tetrachloride was also formed along with a body containing three chlorine-atoms, and another containing five chlorine atoms in the molecule. The two latter substances are probably *monochlornaphthalene dichloride*, $C_{10}H_7ClCl_2$, and *monochlornaphthalene tetrachloride*, $C_{10}H_7ClCl_4$ respectively.

M. M. P. M.

On δ-Nitronaphthylsulphonic Acid and its Derivatives. By P. T. CLEVE (*Bull. Soc. Chim.* [2], xxix, 414).—In a former paper (*ibid.*, xxvi, 444, and this Journal, 1877, i, 469) the author stated that, in the action of nitric acid on β-naphthylsulphonic acid, several isomeric nitro-acids are formed, one of which he then described as β-nitronaphthylsulphonic acid. Further examination of another of these products, which was characterised as forming a soluble barium salt, has shown that it is a mixture of two or three isomerides. From this mixture, an acid, now distinguished as δ-acid, has been isolated by converting the mixture into chlorides in the usual manner, heating the mixed chlorides with carbon bisulphide, and crystallising the undissolved residue from glacial acetic acid.

Pure *δ-nitronaphthylsulphonic chloride* melts at 169°, and crystallises in large well-defined prisms, only sparingly soluble in carbon bisulphide or acetic acid.

δ-nitronaphthylsulphonic acid, obtained by heating the chloride with water in sealed tubes at 130°, forms yellow crystals, which are very soluble. It is a strong acid, and forms well-defined salts, of which the following have been analysed; they are all easily soluble in water:—

Silver salt, $C_{10}H_6(NO_2)SO_3Ag$, yellow needles.

Barium salt, $[C_{10}H_6(NO_2)SO_3]_2Ba + H_2O$, pale-yellow needles.

Lead salt, $[C_{10}H_6(NO_2)SO_3]_2Pb + H_2O$, like the barium salt.

The *potassium salt* crystallises in thin flexible yellow needles.

The *ammonium salt* forms large yellow tables.

The *ethylic ether*, $C_{10}H_6(NO_2)SO_3C_2H_5$, obtained by the reaction of ethyl iodide with the silver salt, crystallises from alcohol in yellow needles, melting at 103° (?).

The *amide*, $C_{10}H_6(NO_2)SO_2NH_2$, crystallises in yellow prisms, which melt at 216°.

The acid is converted by reduction with ammonium sulphide into *δ-amidonaphthylsulphonic acid*, $C_{10}H_6(NH_2)SO_3H$, which crystallises from water in silvery scales. J. R.

Comparison of Oxyanthraflavone with Isopurpurin. By A. ROSENSTIEHL (*Bull. Soc. Chim.* [2], xxix, 405).—The author has made a careful comparison of these two substances, and finds that they are identical in properties. Both are nearly insoluble in benzene; they behave in precisely the same manner with alkalis; their acetyl-compounds are identical in crystalline form and in melting point (220°), and the absorption-spectra of their solutions are perfectly coincident. J. R.

Electrolysis of Glucosides. By M. COPPOLA (*Gazzetta chimica italiana*, viii, 60—71).—*Salicin.*—Lapschin and Tischanowicht, by submitting a solution of salicin to electrolysis with 400 Bunsen's elements (*Jahrb.*, 1861, p. 49), found that it split up into glucose and saligenin, which yielded salicylic aldehyde and salicylic acid, a result confirmed by a preliminary experiment made by the author with a feeble current. A careful study of the decomposition of salicin solution, in which the liquids surrounding the two platinum poles and also the gases evolved there were separately examined, showed that the liquid at the positive pole became much more coloured than that at the negative pole, and had a much stronger acid reaction; similar effects were produced even in a more marked degree when the solution was very feebly acid with sulphuric acid. Neither oxalic, formic, nor acetic acid could be detected amongst the products. When lead poles were used in alkaline solutions, besides salicylic aldehyde and salicylic acid, a quantity of a brownish-yellow substance was formed at the positive pole, and dissolved in the liquid, no gas being evolved; whilst at the negative pole the liquid remained colourless, but gas was evolved in abundance. This brown substance the author believes to be ulmic acid, formed by the decomposition of the glucose. The gas evolved at the negative pole consisted principally of hydrogen (87·88) with a little carbonic anhydride (7·32) and carbonic oxide (4·80); that collected at the positive pole was a mixture of oxygen, carbonic oxide, and carbonic anhydride, with some hydrogen owing to admixture of gas from the negative pole.

Amygdalin.—The decomposition of a solution of amygdalin (with 10 Bunsen cells), as in the case of salicin, proceeds slowly at first, but afterwards more rapidly, the liquid at the positive pole becoming pale yellow. The products of decomposition are glucose, benzoic aldehyde, and hydrogen cyanide: neither oxalic nor formic acid could be detected, but ammonia is formed, derived probably from the hydrocyanic acid, the formic acid produced at the same time being oxidised to carbonic anhydride and water: a portion of the aldehyde also is oxidised to benzoic acid. The gas evolved at the negative electrode was pure hydrogen, whilst that at the positive electrode was a mixture of carbonic anhydride, carbonic oxide, oxygen, and nitrogen.

C. E. G.

Action of Ferric Chloride and Sulphuric Acid on Opium Bases. By D. LINDO (*Chem. News*, xxxvii, 158).—By treating a small quantity of codeine with concentrated sulphuric acid and ferric chloride, a magnificent and intense blue colour, similar to that of ammonia-sulphate of copper, is obtained. Morphine treated in like manner gives rise to an intense *indigo-blue* coloration. A gentle heat must be applied, otherwise no reaction is obtained. D. B.

On Quinine Tannates. By J. JOBST (*Arch. Pharm.* [3], xii, 331—335).—Contrary to what is usually stated, tannic acid does not combine with quinine to form a quinine tannate of definite composition, but a compound in which tannic acid may vary indefinitely, and to an extent depending on the method of preparation.

The following analyses of several so-called quinine tannates show that the alkaloïd varies not only in quantity, but also in character.

No. 1 had been prepared by precipitating a neutral solution of quinine hydrochloride with a solution of ammonium tannate.

Nos. 6 and 7, which the author obtained by adding tannic acid to an acid solution of quinine sulphate, show that quinine tannates can contain tannic acid in very large proportion:—

	Water at 120°.	Quinine.	Quinidine.	Cinchonidine.	Cinchonine.	Total alkaloïd.
	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.
No. 1......	7·2	31·37	—	—	—	31·37
„ 2......	9·7	22·72	—	—	—	22·72
„ 3......	9·1	4·46	11·97	7·33	—	23·76
„ 4......	9·8	4·93	2·43	13·10	3·35	23·82
„ 5......	10·2	6·23	trace	23·80	trace	27·03
„ 6......	10·7	10·00	—	—	—	10·00
„ 7......	11·4	7·40	—	—	—	7·40

The amount of quinine in No. 1 corresponds nearly with that required by the formula, $C_{20}H_{24}N_2O_2.2C_{14}H_{10}O_9 + 4H_2O$, and in No. 2 with $C_{20}H_{24}N_2O_2,3C_{14}H_{10}O_9 + 8H_2O$.

The bitter taste in these tannates decreases as the proportion of tannic acid in them is increased.

The author gives the following method as the best to follow in the analysis of quinine tannate.

One gram is finely powdered, and mixed with milk of lime, then dried, and the dried residue exhausted with chloroform. The residue, after distilling off the chloroform, is dried at 120°, and weighed, then dissolved in dilute sulphuric acid, and tested with ether and ammonia in the usual manner, in order to ascertain whether the alkaloïd is pure quinine, or contains any alkaloïd insoluble in ether, such as quinidine, cinchonidine, or cinchonine. A. J. C.

Some Decompositions of Strychnine. By R. Schiff (*Gazzetta chimica italiana*, viii, 82—83).—Strychnine dissolves in fuming nitric acid, with copious evolution of nitrous fumes, and the solution when diluted yields an amorphous precipitate, which is a mixture of a base with a neutral substance. On dissolving this in glacial acetic acid, and adding water, the neutral substance is thrown down as a yellow amorphous powder, whilst the base remains in solution, and may be precipitated by sodium carbonate. This is also amorphous, and appears to be nitrostrychnine, but attempts to purify it failed.

If the solution of strychnine in nitric acid be heated for some hours, a yellow crystalline compound is deposited as the solution cools, and more may be obtained by adding water to the mother-liquors. It forms yellow plates of the composition, $C_{16}H_{11}N_4O_{15}$, which are soluble in boiling water, and melt above 300° with decomposition. It appears to have acid properties, but no crystallisable salts could be prepared. An amorphous basic substance is produced when strychnine is treated with potassium chlorate and hydrochloric acid. C. E. G.

Action of Reducing Agents on Brucine previously dissolved in Nitric Acid. By R. Röhre (*Deut. Chem. Ges. Ber.*, xi, 741—743). —When a solution of brucine in nitric acid is allowed to stand for some time, and is then treated with stannous chloride, ammonium sulphide, or sulphurous acid, violet-coloured crystals are slowly formed. The composition of these crystals has not as yet been determined (comp., p. 437). M. M. P. M.

On Ergotinine. By Tanret (*Compt. rend.*, lxxxvi, 888—890).—In the first part of this paper details of the preparation of ergotine are given, by which a crystalline and an amorphous product are obtained; the latter has not been analysed. The portion crystallised from alcohol, which was perfectly white, and in needle-shaped crystals, gave numbers corresponding closely with the formula, $C_{35}H_{40}N_4O_6$.

The formula $C_{35}H_{40}N_4O_6.HCl$, requires 5·47 per cent. of chlorine; the chlorhydrate obtained from the crystallised ergotinine gave the author 5·74 and 5·55 per cent. The hydrobromide requires 11·54 per cent. of bromine; found 11·78 per cent. for the product prepared from crystallised ergotinine, whilst that from amorphous ergotinine gave 12·22 and 11·73 per cent. The salts are amorphous, and were obtained by precipitating an acetic solution of ergotinine with an excess of dilute hydrochloric or hydrobromic acid. The sulphate and lactate of ergotinine are the only crystalline salts the author has been able to prepare, but he has not obtained them in sufficient quantity for analysis. J. M. T.

Transformation of Albuminoïds in Cheese and Milk into Fats. By A. W. Blyth (*Analyst*, iii, 230—235).—From experiments made by C. Blondeau on cheese (*Ann. Chim. Phys.*, iv, 1), with reference to the change it undergoes, probably from the influence of mycoderms, the author thinks that from the analysis of milk or cheese, after five or six months' decomposition, it will be possible by calculation to arrive at its original composition. With this idea he has made experiments on the subject, from which it appears that the amount of albuminoïds decreases in milk which has stood for some time, whilst that of fats increases. Lactic fermentation takes place at the same time, by which alcohol, acetic and lactic acids, and ammonia are produced. In every case the milk had an odour of acetic ether. The author's experiments on cheese are not yet completed.

L. T. O'S.

Decomposition of Albumin by Fused Potash. By M. Nencki (*J. pr. Chem.* [2], xvii, 97—105).—The main object of the paper is to show that the body obtained by Kühne (*Ber.* viii, 206), and by Engler and Janecke (*Ber.* ix, 1411), by fusing albumin with potassium hydrate, and which the latter named *pseudoindol*, is not a single substance, but a mixture of indol and the body obtained from fæces in the author's laboratory, to which the name of *skatol* has been given.

The author finds that when fused potash acts on albumin, leucine and tyrosine are formed, in addition to peptones, and that by further action, volatile fatty acids, especially valeric acid, are produced, with evolution of hydrogen: simultaneously indol and skatol are formed. If the fusion is continued for a long time, the amount of peptone-like bodies decreases, and the leucine and valeric acid are gradually converted into butyric acid. The tyrosine is perfectly decomposed, and phenol appears instead. The latter body is probably formed from the tyrosine, since whenever phenol was produced, whether by putrefaction or by the action of potash, tyrosine was wanting, and *vice versâ*.

See the author's article "Eiweisskörper," in the *Neues Handwörterbuch der Chemie*. G. T. A.

Presence of Urea Ferment in the Air. By P. Miquel (*Bull. Soc. Chim.* [2], xxix, 387—397).—The conversion of urea into ammonium carbonate was first attributed by Pasteur to the action of a peculiar organised ferment. Musculus, on the other hand, maintained that ammoniacal fermentation is due to a soluble mucus contained in the urine. The author has made a large number of experiments on this subject, of which details are given in the present paper. His results are confirmatory of Pasteur's observations. Urine sterilised by boiling for a quarter of an hour, and then sealed up, may be kept for any length of time without undergoing ammoniacal fermentation. But when such sterilised urine is exposed to the air, or when a small portion of dust from the air, or of water which has been agitated with air in the neighbourhood of a foul urinal is introduced into it, the ammoniacal fermentation is almost invariably set up. Ammoniacal fermentation is always attended with the development of peculiar microscopic organisms, as stated by Pasteur. J. R.

Action of Hydriodic Acid on Olivil. By D. AMATO (*Gazzetta chimica italiana*, viii, 83—86).—Pure olivil (m. p. 119—120°) obtained from olive-gum was digested with concentrated hydriodic acid (b. p. 127°) for one hour. A mixture of ethyl and methyl iodide was formed, and a solid non-volatile black substance, of glistening aspect. This is insoluble in water, only slightly soluble in ether, but readily in alcohol, especially when hot. It is reprecipitated from the alcoholic solution on addition of water. The author intends to investigate the nature of this substance. C. E. G.

Chemistry of Vegetable Physiology and Agriculture.

Absorption of Water by Plant Roots. By J. VESQUE (*Chem. Centr.*, 1878, 165).—The author's investigations show that the transpiration effected by leaves depends not only on the surface area, but also upon the age of the leaves. Experimenting with *Helianthus tuberosus*, he found that the transpiration increased rapidly with increase of surface, from the youngest to the eleventh leaf, but that it increased but slowly from that leaf to the seventeenth, after which it became stationary, although the surface of leaf exposed continued to increase.

Increase of temperature causes a decrease in the absorption of water by the roots. Decrease of temperature has an opposite effect. The absorption by the roots is not proportional to the temperature of the leaves when these are exposed to a non-saturated atmosphere. Dark heat-rays exert a marked influence on absorption when the leaves are in a dry atmosphere, acting in the same manner as a rise of temperature. M. M. P. M.

Presence of Sodium in Plants. By C. COUTEJEAN (*Compt. rend.*, lxxxvi, 1151).—The author has examined, by means of the gas blowpipe, about 600 species of plants, and has come to the following conclusions :—

More than three-fourths of terrestrial (non-maritime) plants contain sodium. The sodium is contained in largest quantity in the underground parts of the plants, and the quantity decreases in the higher parts, so that the flowers, the upper part of the stem, and upper leaves contain little or none, whilst the base of the stem, the lower leaves, and the root contain a notable quantity. Aquatic plants contain sodium in all their submerged parts in nearly equal proportion, whilst the parts above the surface of the water follow the same law as land plants. Plants growing in wet places and in marshes, &c., are richer in sodium than plants growing on dry land, especially in their subterranean parts.

The proportion of soda varies according to the order, genus, and species of the plant. Generally those plants which contain much nitrogen contain very little sodium.

Non-saline soils free from lime seem more favourable to soda-loving plants than calcareous soils. It remains to be determined whether the medium acts by itself, if the soil is calcareous or granitic, or if soda-loving plants seek clay and granite because these soils, being impervious, collect stagnant water and form marshes. The author prefers the latter view, for none of these soils shows any trace of sodium when examined spectroscopically.

In maritime plants, even though soda is present in large quantity in most parts, the flower is never found to contain the smallest trace of this substance.

All the above facts support the opinion that soda is useless, if not hurtful to most plants. The roots of land plants and the submerged parts of aquatic plants absorb soda without selection, and it is but partially transferred to the upper parts. The proportion of soda in all aquatic plants is also found to be practically the same.

C. W. W.

Silicon Compounds in Plants. By W. LANGE (*Deut. Chem. Ges. Ber.*, xi, 822—826).—A concentrated aqueous extract of *Equisetum hiemale*, from which the albuminoïds have been removed by boiling, yields a gelatinous precipitate on the addition of lime water in excess. The precipitate, which consists essentially of magnesium metasilicate and magnesium hydrate, mixed with a small quantity of alumina and ferric oxide, is soluble in acids. A similar precipitate of magnesium hydrate and metasilicate is formed when lime water or caustic potash in excess is added to a mixture of magnesium sulphate and a very dilute solution of silica in hydrochloric acid. Since the fresh sap of the plant has an acid reaction, the author considers that the silicon must be present in the form of a very dilute solution of silica hydrate.

Since cellulose, which has been repeatedly dissolved in an ammoniacal solution of copper oxide and reprecipitated by hydrochloric acid, with the object of purifying it from inorganic matter, still yields 0·079 per cent. of ash, containing 50 per cent. of silica, it is in the author's opinion probable that the silicon is present in the membranes of the plants in a very finely divided but insoluble state.

W. C. W.

Analytical Chemistry.

Determination of Sulphuric Acid in Urine. By E. BAUMANN (*Analyst*, iii, 240).—This method is based on the fact that "sulphuric ethers" existing in urine are not decomposed when gently heated with acetic acid, but are readily decomposed when heated with a small quantity of hydrochloric acid. The sulphuric acid present as salts is determined by mixing 25 to 50 c.c. of the urine with acetic acid, and adding an equal bulk of water and excess of barium chloride. The whole is heated on a water-bath for three-quarters of an hour, and the baric sulphate collected and weighed. The filtrate from this is boiled with hydrochloric acid until the precipitate separates out completely, when it is filtered and washed with hot alcohol to remove resins, &c., which are thrown down at the same time. This gives the amount of sulphuric acid as ethers; the former precipitate the amount as salts.

L. T. O'S.

Action of Potassium Chlorate on the System. By O. HEHNER (*Analyst,* iii, 236—240).—When potassium chlorate is administered, about 94 per cent. of it passes out of the system in the urine, but whether the other 6 per cent. is decomposed in the body or is evacuated with the fæces the author is unable to decide. In order to estimate the amount of chlorate in the urine, the author tried the method of reduction with the copper-zinc couple, but the process was unsatisfactory, from the frothing of the liquid and the long time required for complete reduction. An eminently satisfactory and simple method, however, is to precipitate the chlorides in a measured quantity of the urine with excess of silver nitrate, and after removal of the silver chloride, to render the filtrate acid with sulphuric acid, and add metallic zinc. If the liquid be gently warmed, the reduction is complete in about half an hour, and the hydrochloric acid produced may be estimated in the clear liquid in the usual way. A very good qualitative test is to add an acid solution of ferrous sulphate to the solution after removal of the chloride as above. On heating, the chlorate is reduced, and silver chloride is thrown down. C. E. G.

Analysis of American Moulded Glass. By CAPLAN (*Dingl. polyt. J.*, ccxvii, 509).—Caplan gives the following as the composition of American beer glasses sent to Berlin :—

SiO_2	75·00
Fe_2O_3	0·19
Al_2O_3	0·11
MnO	0·38
CaO	5·18
MgO	0·52
Alkalis (Na_2O) and residue	18·62
	100·00

A direct alkali estimation gave 18·52 per cent. Na_2O.

According to A. Frank (*Töpfer und Zieglerzeitung*, 1877, 366), the American glass has a specific gravity of 2·486, and is very fusible.

J. T.

New Method for the Decomposition of Chromic Iron. By E. F. SMITH (*Am. J. Sci.* [3], xv, 198—200).—Chrome iron ore when very finely divided is completely decomposed by heating it with bromine under pressure. The sample should be ground and elutriated. A considerable quantity of bromine water and from 10 to 12 drops of bromine should be used. The mixture should be heated at 180° for two or three days in a sealed tube.

Chromic oxide, prepared by the ignition of the hydrate, may be brought into solution by digestion with bromine and sodium hydrate solution in a beaker. M. M. P. M.

Detection of Alcohol in Ethereal Oils. (*Chem. Centr.*, 1878, 208).—A given volume of the oil to be tested is shaken up with its own volume of pure glycerin. When the liquids have completely separated, the increase in the volume of the glycerin is determined. This increase represents the amount of alcohol contained in the oil. M. M. P. M.

Adulteration of Milk with Glycerin. By J. Muter (*Analyst*, iii, 235—236).—It is possible to adulterate milk with 35 per cent. of glycerin-water, sp. gr. 1·03, without the possibility of detection by the "gravity" or "solids not fats" methods. The following modification of Wanklyn's process has been devised by the author to meet this case. The residue, which is determined as usual by evaporation and extraction with ether, is treated with a mixture of equal volumes of alcohol and ether, and the residue left after the evaporation of the extract is tested for glycerin. If this substance should be found, a complete analysis of the milk must be made, and both sugar and casein estimated. The difference between the true and apparent "solids not fats" will be glycerin. L. T. O'S.

Diseased Milk. By C. Heisch (*Analyst*, iii, 249—251).—The first sample showed no peculiarities on analysis, but when examined under the microscope was found to contain Blyth's bodies (*Analyst*, i, 239), pus and blood corpuscles, and pieces of skin tinged with blood. The following are two samples of milk, and one of cream, obtained from a mixture of the milk of the two cows (suffering from foot-and-mouth disease) which had yielded the milk.

The results of the analysis of the milk are—

	(1).	(2).
Total solids	13·97	10·54
Solids not fats	9·61	9·64
Fat	4·35	0·90
Ash	0·71	0·60

On microscopical examination, No. 1 showed Blyth's bodies and blood-corpuscles, the blood-bands being distinctly seen in the spectroscope; and No. 2 showed colostrum and blood-corpuscles, which was confirmed by the spectroscope.

The cream had a peculiar reddish colour, and all the appearances described, in a marked degree.

Two more samples of milk from the same cows a week later gave on analysis the following results:—

	(1).	(2).
Total solids	17·77	12·86
Solids not fats	9·60	7·82
Fat	8·17	5·04
Ash	0·68	0·82

In No. 1 the microscope showed a few of Blyth's bodies; the blood bands were scarcely visible. In No. 2 colostrum was still present, and casts of the mammary glands; the blood-bands were visible.

L. T. O'S.

Diseased Milk. By G. W. WIGNER (*Analyst*, iii, 251—254).—The milk in question, although it gave satisfactory analytical results, was yet found on microscopical examination to be unfit for human food. The milk was allowed to stand for six days, and examined on the first, second, third, and sixth days. On the first day it contained pus and blood-corpuscles, and Blyth's bodies, which are contained in milk yielded by cows suffering from foot-and-mouth disease.

On the second day it contained blood-corpuscles, Blyth's bodies, and skin streaked with blood. It had partially solidified, as colostrum milk solidifies when boiled. The cream also had become mottled, and the surface corrugated.

On the third day there appeared to be only a few Blyth's bodies, the surface of the cream was covered with a fungus, and the whey had separated from the curd in vertical streaks.

On the sixth day the milk had so decomposed, that for practical purposes the examination was useless.

The necessity of a microscopical examination is clearly seen from this case.

L. T. O'S.

Butter Analysis. By F. P. PERKINS (*Analyst*, iii, 241).—The following is a method for estimating the volatile acids in butter. The fats are saponified and allowed to cool, the insoluble acids precipitated by dilute sulphuric acid, and the clear liquid passed through a weighed filter-paper. The fat in the flask is washed by agitation with hot water, which is allowed to cool, and is then poured on the filter-paper (this operation is repeated several times); the insoluble acids are dried at 110° and weighed. The filtrate is made up to half a litre, the total acidity in 100 c.c. of which is determined by means of a decinormal caustic potash solution. Another 100 c.c. are evaporated to 10 c.c., water added, and the acidity again determined. The difference between the two numbers multiplied by 5 gives the acidity due to volatile acids in c.c. of KOH. The method gives fair results.

L. T. O'S.

Butter Analysis. By C. JEHN (*Arch. Pharm.* [3], xii, 335—337).—The maximum amount of insoluble fatty acids in pure butter has been regarded by Hehner and other chemists to be 88 per cent.; but from the results of ten experiments, in which the amount of insoluble fatty acids varied between 86·2 and 89·8 per cent., the author considers the maximum to be nearer 90 per cent.

It is to be remarked, however, that this maximum limit has been based on the higher results, which were obtained by weighing the fatty acids after first melting them with wax, according to the method of Dietzsch. E. Reichardt, in noting the fact in an addendum to this paper, states that he has found 86—87 per cent. of fatty acids in butter.

A. J. C.

Test for Reducing Substances, especially Glucose. By E. POLLACCI (*Gazzetta chimica italiana*, viii, 80—82).—It is proposed to employ ferric oxide instead of cupric oxide, as a test for substances, such as glucose, which exert a reducing action. A minute quantity of a solution of pure ferric oxide is added to a little distilled water by means of a glass rod, then 3 or 4 drops of soda-solution, and finally the liquid to be tested. The whole is boiled for a minute or two; sulphuric acid is added in quantity sufficient to dissolve the iron oxide, and then a drop of potassium ferricyanide solution: a blue precipitate is produced immediately if the liquid tested had contained any reducing substance. In this way 1 part of glucose in 25,000 of water may be detected. Cane sugar does not produce this effect.

C. E. G.

Tests for Glucose. By G. MAZZARA (*Gazzetta chimica italiana*, viii, 86—87).—The author mentions that nickel sesquioxide is reduced to the monoxide by glucose in presence of alkalis, and that iodic acid, under similar circumstances, yields an alkaline iodide. Neither of these reactions, however, can be used for quantitative determinations.

C. E. G.

Reduction of Alkaline Copper Solutions by Saccharine Bodies. By F. SOXHLET (*Chem. Centr.*, 1878, 218—224, 236—240).—The author shows by numerous experiments that—1. The supposition that 1 equivalent of grape or of inverted sugar reduces 10 equivalents of copper oxide is false. 2. The reducing action of sugars on alkaline copper solutions cannot be expressed by an equivalent proportion, since the amount of copper oxide reduced varies with the strength of the copper solution. This proportion is found to vary from 1 : 8·5 to 1 : 12·5. 3. The results obtained with Fehling's solution by titration are purely empirical; they are very exact, being to ± 0·2 per cent., when made under the same conditions as to concentration. Undiluted Fehling's solution gives with 1 per cent. sugar solutions 0·5 per cent. higher results than with $\frac{1}{2}$ per cent. solutions; fourfold diluted Fehling's solution gives the same results with both strengths of sugar solution. The results obtained with Fehling's solution, diluted with four volumes of water, differ by 3 per cent. from those obtained by Fehling (*Ann. d. Chem. u. Pharm.* lxxii, 106), and confirmed by Neubauer (*Arch. du Pharm.* [2], lxxi, 278; the undiluted solution gives results differing by 4 per cent. as compared with the diluted one. 4. The gravimetric method always gives higher numbers than the volumetric, unless care be taken that the copper solution employed be not more than from 0·5 to 1·0 per cent. in excess: hence, *a gravimetric estimation of sugar by means of an alkaline copper solution is quite impossible.* The author strongly criticises some apparently exact results obtained by experimenters using the gravimetric method. Considerable error may be introduced by heating Fehling's solution for some time, as the undiluted solution cannot be heated for 15 minutes without precipitating some suboxide of copper.

Milk sugar does not decompose the copper solution as quickly as grape sugar, so that it is necessary to heat somewhat longer; six to seven minutes is enough, otherwise it cannot be so well titrated as the other; but the estimation of milk sugar can be made more exact than in the case of grape or inverted sugar, as the former either in $\frac{1}{2}$ per cent. or 1½ per cent. solution reduces the same amount of oxide in diluted and undiluted Fehling's solution. Six experiments gave the following results:—

1 gram of milk-sugar reduces—

In ½ per cent. solution 147·8 c.c.; Fehling's solution = 1·3023 gr. Cu = 7·39 equivalents.

In 1½ per cent. solution 147·9 c.c.; Fehling's solution = 1·3031 gr. Cu = 7·39 equivalents.

In 1½ per cent. solution 148·0 c.c.; Fehling's solution = 1·3040 gr. Cu = 7·40 equivalents.

The author always adds 50 c.c. of 1 per cent. sugar solution, or double that amount of the ½ per cent. solution to a measured volume of Fehling's solution previously mixed with an equal volume of Seignette salt solution, and heated to boiling. After boiling for 6—7 minutes in the case of milk-sugar, and for 3—4 minutes in the case of grape or inverted sugar, the solution is filtered, and a portion is acidified with acetic acid, and tested for copper with potassium ferrocyanide. This process is repeated until the exact amount of copper solution is obtained.

By gravimetric analysis, 1 : 7·4 and 1 : 7·67 were the proportions of milk sugar to copper oxide obtained.

The behaviour of maltose and lactose to Sachsse's alkaline mercury-iodine solution has been examined, and Sachsse's results confirmed. Milk-sugar and grape-sugar behave relatively towards Sachsse's solution as they do towards Fehling's solution. J. T.

Estimation of Calcium Tartrate in Crude Tartars. By A. SCHEURER-KESTNER (*Compt. rend.*, lxxxvi, 1024—1025).—The ordinary method of estimating calcium tartrate, by precipitating a solution of the crude tartar in hydrochloric acid with caustic soda, does not give correct results in presence of calcium sulphate, as the calcium sulphate and sodium tartrate undergo double decomposition, forming calcium tartrate and sodium sulphate.

To avoid this source of error, it is proposed to dissolve the tartar in hydrochloric acid, and to precipitate the whole of the tartaric acid, as calcium tartrate, by the addition of calcium chloride and caustic soda. The precipitate is washed, dried, and calcined, and the resulting calcium carbonate estimated by titration in the usual way.

Another portion of the tartar is treated with hot water, and the solution is titrated with standard soda. From these data the amount of calcium tartrate and of potassium bitartrate in the crude material can be calculated. W. C. W.

Tannin Estimation. By F. KATHREINER (*Dingl. polyt. J.*, ccxxviii, 53—64).—From experiments made on Löwenthal's method, the author concludes that:—1. The permanganate solution should not contain more than 1·33 grams of the crystallised salt per litre. 2. The indigo solution should be such that 20 c.c. = 10 c.c. of permanganate. 3. The solution of gelatin and sodium chloride (25 grams gelatin dissolved in water, saturated with pure sodium chloride and made up to 1 litre with a saturated solution of salt) should be kept well corked, and filtered before using. 4. The concentration of the tannin solution should be such that 10 c.c. may require about 6 c.c. of permanganate solution.

To determine the "non-tannin" constituents oxidisable by the permanganate, 50 c.c. of water containing 2·5 grams of sulphuric acid are added to 100 c.c. of the solution, stirred up with 100 c.c. of the gelatin solution, and after standing all night, the solution is filtered, and a measured portion of the filtrate is titrated.

The time required for titrating is about four minutes for the original solution, and about six minutes for the "filtrate."

The author recommends Löwenthal's method, and cites other opinions in its favour; he criticises unfavourably Hammer's method, and condemns Clark's and Jean's methods. J. T.

Codeine Reaction. By O. HESSE (*Arch. Pharm.* [3], xii, 330).—As already shown by the author (*Ber.*, iv, 697), codeine forms a colourless solution with *pure* concentrated sulphuric acid, and a blue solution with sulphuric acid containing iron, *e.g.*, ferric chloride. On account of the slow action of the acid on crystalline codeine, it is recommended, in this test, to employ codeine which has been dried in a desiccator: 1—1½ c.c. of sulphuric acid added to 2—3 milligrams of the finely-powdered codeine, gives a colourless solution.

The pink colour obtained by Calmberg (this Journal, 1876, i, 778), when codeine was moistened with concentrated sulphuric acid, was probably due to impurities in the acid, as codeine is thereby more or less coloured. A. J. C.

A New Creatinine Reaction. By O. MASCHKE (*Zeitschr. Anal. Chem.*, 1878, 134—141).—On the addition of an excess of soda, potassium-sodium tartrate, and copper sulphate to a dilute solution of creatinine, a cloudiness is produced, which, after a short time, settles as a white precipitate. This reaction is hastened by heating the solution to 50—60°; if, however, the solution be boiled, gradual decomposition ensues. This reaction is sufficient to detect 0·01 gram in 100 c.c. of solution, but the precipitate, which is a compound of creatinine with cuprous oxide, is formed at the cost of some of the creatine present; so that it is advisable to add grape-sugar, which reduces the copper salt in place of the creatinine. The precipitate is soluble in water and in ammonia, the solution becoming blue on exposure to the air. From the copper salt the compound of creatinine with zinc chloride may be formed.

Very small quantities of sugar may be detected in urine, by precipitating the uric acid with an alkaline copper solution, then adding Rochelle salt and a little sulphate of copper, filtering, and allowing the clear liquid to flow from a pipette on to the surface of a boiling-hot solution of soda. A clear, yellowish-brown ring, which gradually becomes cloudy, is formed at the line of contact of the two solutions. This appears to be due to the united actions of sugar, urochrome, and creatinine present, producing a double compound of creatinine and cuprous oxide with urochrome and cuprous oxide. Indican does not appear to be capable of forming a brown ring, but rather to hinder the precipitation of cupric and cuprous oxides. On the contrary, creatine gives no precipitate when treated as above. E. W. P.

Technical Chemistry.

Action of the Glover Tower. By F. HURTER (*Dingl. polyt. J.*, ccxxvii, 563—570).—From the books of Messrs. Gaskell, Deacon, and Co., it appears that per 100 of burnt sulphur—(1) the amount of nitre in circulation through the system connected with seven Glover towers was 19·61; (2) the amount of nitre added was 5·04; (3) the mechanical loss was 0·58, or 11 per cent. of the newly-added nitre; and the loss by chemical decomposition was 4·45, or 89 per cent. of the added nitre, and 22·75 per cent. of the nitre in circulation. The author is convinced that the greater half of this decomposition takes place in the Glover tower, for the conditions are much more favourable there than in the chamber. Laboratory experiments were made to determine the amount of loss due to chemical decomposition. An artificial nitrose was prepared by heating lead nitrate and passing the fumes into sulphuric acid; and the amount of nitric trioxide and tetroxide contained in it was determined. Mixtures of sulphurous anhydride and oxygen, or of sulphurous anhydride and air, in definite quantity, were passed through. The results show that the loss of nitre per 100 of SO_2 increases with the temperature, and at the same temperature the loss increases as the amount of oxygen in the gas mixture diminishes. J. T.

Glass containing Alkaline Bases only. By P. EBELL (*Dingl. polyt. J.*, ccxxviii, 47—51).—Certain kinds of glass can be coloured yellow to brown by the addition of sulphur, whilst others containing less alkali cannot thus be coloured. The boundary between these is well defined.

The following mixtures were fused, well stirred up and treated with pieces of sulphur.

	a.	*b.*	*c.*
SiO_2	160	150	130
K_2CO_3 ..	138	138	138

After cooling, *a* was colourless; *b* showed yellow colour in spots, whilst *c* was deep brownish-yellow throughout. Evidently *b* lay near to the boundary. Analysis of the glass *b* gave the relation $K_2O : SiO_2 = 1 : 2·67$, which approaches very closely to that found for lime and baryta glasses, viz., base : $SiO_2 = 1 : 2·5$ (*ibid.*, ccxxv, 70). With this relation of base to acid the silica seems to be saturated.

As the proportion of silica is increased, the fusibility of the glass diminishes, and the glass becomes more and more like fused quartz, the excess of silica separating out in a crystalline form. When cooled quickly, the glass rich in silica has a bright lustre; when slowly cooled on the contrary, it becomes devitrified, at least when it contains about 88 per cent. of silica. To ascertain if the portion separated out was silica, the following mixtures were fused:—

	a.	*b.*	*c.*
Sand	200	200	200
K_2CO_3 ..	150	100	50

The first two fused easily and could not be devitrified by slow cooling. *c* fused after long heating, and on cooling slowly was completely devitrified. Numerous aggregates of crystals resembling wavellite appeared, but no individual crystals could be made out. The glass absorbs water and carbonic anhydride from the air, and becomes covered with an efflorescence of potassium carbonate.

On treating with acid, and subsequently with sodium carbonate, a crystalline residue was obtained, which yielded 99·53 per cent. of silica. Hence pure silica crystallises out from these acid glasses. The same mixture *c*, when quickly cooled, does not absorb moisture and carbonic anhydride from the air, and on decomposing with an acid no crystalline residue remains. The slowly cooled glass contained $SiO_2 = 84·12$ per cent., and $K_2O = 15·88$ per cent.; also 55·99 per cent. of silica was in the crystalline form, leaving 28·13 per cent. combined with the potash; this corresponds to $K_2O : SiO_2 = 1 : 2·77$. This is very nearly the same as that obtained with the neutral glass previously mentioned. J. T.

Refining of Sugar by the Use of Alumina. By O. Kohlrausch (*Chem. Centr.*, 1878, 185—191).—The author's experiments upon the method introduced by Löwig for refining sugar, show that by the use of moist aluminium hydrate a nearly colourless liquid, yielding a crystalline mass on evaporation, may be obtained from raw sugar, but that the whole of the colouring matter cannot be removed without the use of animal char, and that the formation of molasses cannot be entirely prevented. The aluminium hydrate is not, according to the author, completely insoluble in the raw syrup.

The large mass of moist hydrate which it is necessary to employ, militates against the economical application of Löwig's process.

M. M. P. M.

Burning of Bricks in Annular Kilns. By F. Fischer (*Dingl. polyt. J.*, ccxxvii, 65—69).—The author gives, in the first portion of this paper, details respecting the early history of brick-making, after which he describes the qualities of various kinds of clay used for this industry. The following analysis gives the composition of kaolins used for the manufacture of bricks :—

Constituents.		Kaolin of Ledetz.	Kaolin of Kottiken.	Kaolin of Tremosna.	Kaolin of Zettlitz.	Kaolin of Lettin.	Kaolin of Kaschkan.	Kaolin of Sennewitz.	Mass of the Royal Porcelain Manufacture.
Clay		88·26	87·41	90·29	96·55	74·09	78·51	63·77	54·92
Quartz		3·08	6·40	4·08	2·30	17·21	20·90	35·50	23·52
Felspar		8·66	6·19	5·63	1·15	8·70	0·59	0·73	21·56
Clay.	Silicic acid	45·36	44·76	45·98	45·36	45·63	45·00	45·30	45·46
	Alumina	39·58	39·65	39·36	39·71	38·08	39·32	37·15	37·35
	Ferric oxide	0·92	0·72	0·73	1·13	0·88	0·75	1·29	1·07
	Magnesia	0·20	0·34	0·45	—	0·66	0·28	0·78	0·73
	Potash	0·21	0·02	0·99	1·24	1·84	0·53	2·02	2·57
	Water	14·02	14·07	13·28	13·32	13·32	14·20	13·11	12·74

The following analyses give the composition of French and German plastic clays: (1) White clay from Ebernhahn; (2) ditto from Baumbach; (3) ditto from Bendorf; (4) ditto from Laemmersbach; (5) ditto from Höhr; also (6) a French clay, meagre, and (7) a French clay, fat:—

Constituents.		1.	2.	3.	4.	5.	6.	7.
Clay		71·22	76·30	39·71	66·23	54·73	44·63	71·54
Quartz		24·03	22·40	57·15	31·42	41·77	52·77	25·97
Felspar		4·75	1·30	3·14	2·35	3·50	2·60	2·49
Clay.	Silicic acid	46·62	47·44	47·44	47·39	47·45	45·99	45·75
	Alumina	36·01	37·21	35·74	36·40	37·88	38·08	35·77
	Ferric oxide	1·39	1·68	1·94	1·52	1·41	2·44	2·94
	Lime	—	trace	trace	—	—	trace	—
	Magnesia	0·73	0·79	0·88	0·51	0·71	1·19	0·78
	Potash	3·47	4·22	3·85	3·96	4·08	2·36	1·24
	Loss by ignition	10·19	9·69	9·52	9·92	9·00	10·76	13·70

Seger mentions that it is not possible to distinguish the differences observed in the degree of plasticity of clays by their chemical composition; it is, however, more probable that the degree of plasticity is dependent on the structure of the rock from which the clay originates.

The above clays lose their water-contents, partly on being dried, whereby they show a linear shrinking of 11·5 p. c., partly at a higher temperature. In the latter case the clay is converted into a rocky, very porous and friable mass.

In the conclusion of this paper, two tables by Daube are given, illustrating in No. 1 the loss in weight and volume which clay sustains through being dried or heated strongly, and in No. 2 the results of some experiments which tend to show how very much the porosity and resistance of bricks made from the same clays depend on the temperature at which the burning takes place :—

TABLE No. I.

	Loss of weight.	Total Linear Shrinking.
	Per cent.	Per cent.
After drying in the air for one day	11·7	5·0
" " two days	16·1	5·6
" " twenty days	19·8	6·4
After drying at 150°	22·0	6·7
After burning, slightly burnt (red)	28·4	6·7
" medium hard	29·0	6·9
" hard (white)	29·6	—
" to clinker (green)	29·6	8·8

TABLE No. II.

	Burnt slightly.	Burnt medium.	Burnt hard.	Clinker.
	Per cent.	Per cent.	Per cent.	Per cent.
Absorption of moisture in the air	0·4	0·08	—	—
" when dipped into water	16·2	16·5	16·4	1·6
" in boiling water	18·0	19·3	19·0	2·6
Portion soluble in water ($CaSO_4$)	0·7	0·2	0·15	0·09
Loss of weight in 10 p. c. hydrochloric acid	8·5	8·0	7·4	2·5
" in nitric acid	5·0	4·9	4·0	0·6
Increase in weight in sulphuric acid by formation of $CaSO_4$	1·2	1·2	0·9	0·8

D. B.

General and Physical Chemistry.

Refraction of Organic Bodies in the Gaseous State. By MASCART (*Compt. rend.*, lxxxvi, 1182—1185).—This paper gives some results of an investigation of the refraction of gases by a method already described (p. 359 of this volume). The author has examined members of the methyl series, of the ethyl series, and several other bodies, all boiling below 100°.

The specific refraction of a *mixture* of gases is equal to the sum of the refractions of the constituents. This law, however, is known not to obtain for *compounds*, and the author's results confirm this. He finds in general that the observed specific refraction is less than that calculated on the above supposition. If it were true for compounds, bodies with the same elementary composition and volume should have the same specific refraction. This sometimes obtains, as in the case of benzene and acetylene, but not generally. If the law were strictly true, we should be able to calculate the specific refraction of hydrogen, carbon, chlorine, &c.; but in this way very discordant values are obtained, except when homologous compounds of two different series are compared. It would seem, therefore, that no method founded on the consideration of its elementary composition, will enable us to calculate the refraction of a gaseous compound from that of its constituents.

J. H. P.

Absorption-bands of Water, Petroleum, Ammonia, Alcohol, and Glycerin. By J. L. SCHÖNN (*Ann. Phys. Chem. Ergänzungsband*, viii, 670—675).—On examining, by a direct-vision spectroscope, the light from a petroleum lamp, after transmission through 3·8 meters of distilled water, the author observed two absorption-bands between C and D. A thickness of 1·9 meter of common petroleum absorbed all the blue and violet rays, and showed two closely contiguous absorption-bands also between C and D. Several absorption-bands were also observed in the light transmitted through columns of concentrated ammonia solution, alcohol, and glycerin respectively. R. R.

Conductivity for Heat of Rocks and Woods. By E. LESS (*Ann. Phys. Chem. Ergänzungsband*, viii, 517—555).—The method by which the author made his determinations consisted in applying a nearly uniform temperature to the upper surface of a circular plate of the substance, and when a state of equilibrium had been attained, the amounts of heat passing through the different substances were compared by means of a thermo-pile placed at determinate distances below the plate. The heat was applied by means of a copper box through which steam was passed; and to ensure perfect contact, the bottom of the copper box was covered with a stratum of mercury. In like manner a thin disc of copper, applied to the lower surface of the plate, had mercury spread on its upper surface, and means were provided for pressing the surfaces closely together. The effect of the radiation on the thermo-pile was observed when the distances between the face of the latter and the upper disc were severally 63, 73, 83, 93, and 103 millimeters, the exact temperature of the copper box being at the same time ascertained by means of a delicate thermometer. The radiation took place in a chamber from which the air had been exhausted, and means were adopted for maintaining the walls of the chamber at a constant temperature.

The author gives the relative conductivity of a number of rocks from specified localities, and of certain kinds of wood cut in various directions with respect to the fibres and annual rings. For example, marble from the Pyrenees being 1,000; Italian marble is 763; sandstone, 701; slate, 537; common clay, 275; oak in a direction parallel to the fibres, 161; oak, parallel to the fibres and perpendicular to the annual rings, 86; oak, perpendicular to the fibres and rings, 75. The general results are, that crystalline rocks conduct better than those formed of mechanical mixtures, and the fine-grained rocks better than the coarse-grained; the greater conductivity of woods in the direction of their fibres, which has been observed by Tyndall and others, is confirmed.

R. R.

On the Temperature of Flame. By F. ROSSETTI (*Gazzetta chimica italiana*, viii, 121—127).—This is a continuation of the author's former communication on the same subject (*ibid.*, vii, 422, and this vol., p. 467). When a gas flame is used, and the pressure of the gas is varied, the temperature increases but very slightly with the pressure for the same part of the flame (not more than 20°), although the size of the flame may vary greatly.

1. *Luminous Gas Flame.*—The flame of a Bunsen burner of which the air holes are closed, consists of an obscure internal nucleus and an outer luminous envelope, which at the lower part is surrounded by an external zone of a pale-blue colour. The internal cone has a temperature of 280° at its base which gradually increases towards the apex, where it is the same as that of the luminous envelope: this is sensibly constant and about 1050°: the blue portion has a temperature of about 1300°.

In the ordinary fish-tail or bat's-wing burner the edges of the flame are about 1100°, and in the most luminous part 1150°.

2. *Non-luminous Flame.*—The temperatures of the different layers in a Bunsen flame are slightly different from those given in the former paper, namely, 1360° for the external layer, and 1263° for the violet-coloured layer immediately beneath this.

3. In Bunsen's apparatus for showing the absorption of the yellow sodium light by sodium vapour, two flames are employed, the one having a much higher temperature than the other; these were found to be 940° and 1290° respectively.

4. *Flame of a Stearin Candle.*—The blue zone at the lower part of the flame is about 770°; the interior obscure cone 640° at the summit of the wick, and 840° at the apex: the external luminous envelope has a temperature of about 940°.

5. *Flame of a Locatelli Lamp.*—At the base of the flame, just above the wick, the temperature is 575°; the apex of the internal obscure

cone, 875°; the luminous envelope at the same level, 890°; apex of luminous envelope, 920°.

6. *Flame of a Petroleum Lamp.*—This flame, with a chimney, has a temperature of 1030° in the luminous part; without a chimney, 780° in the smoky part; 920° in the most luminous part.

7. *Alcohol Flame.*—The temperature of this flame varies from 900° at the base to 1180° at the apex. The proportion of water present, within certain limits (sp. gr. of alcohol ·912 and ·8225), does not materially influence the temperature.

8. *Mixture of Gas and Air.*—Such a mixture in known proportions was burned in a Bunsen lamp, the air-holes being closed. I gives the temperature obtained with equal volumes of gas and air; II, one vol. gas to two of air; III, one vol. gas to two and a half of air; IV, one vol. gas to three of air.

	I.	II.	III.	IV.
Apex of flame........	1150°	1260°	1150°	1116°
Base of internal cone..	570	330	270	240

A mixture of one vol. gas to four of air could not be burned in a Bunsen lamp, but with an ordinary steatite burner it gave a temperature of 930°. It will be seen that the highest temperature was obtained with a mixture of two vols. air to one of gas; the mixture in a Bunsen burner, under ordinary conditions, was found to be in the proportion 2·2 : 1.

9. *Mixture of Gas and Nitrogen.*—The conditions of experiment were the same as those in 8. I gives the temperature at the apex of the luminous flame; II, that at the base of the internal cone.

		I.	II.
Gas to nitrogen	= 2 : 3	1240°	345°
	= 1 : 1	1180	260
	= 1 : 2	1150	240
	= 1 : 2·5	1080	”
	= 1 : 3	1040	210
	= 1 : 4	960	160

When the proportion of nitrogen to gas exceeds 2 : 1, the flame is no longer luminous.

10. *Mixture of Gas and Carbonic Anhydride.*—With this mixture the space intervening between the flame and the top of the burner is distinctly marked: I and II have the same signification as in 9.

				I.	II.
Gas to carbonic anhydride		= 2	1	1190°	280°
”	”	3	2	1170	270
”	”	1	1	1100	270
”	”	2	3	1020	270
”	”	1	2	880	”
”	”	1	3	780	250

A comparison of the results in 9 and 10 shows that for equal volumes, carbonic anhydride has a more powerful cooling effect on the flame than nitrogen; this is in accordance with the specific heats of the two gases, which are in the proportion of 100 : 71.

The author also describes an electric pyrometer of carbon and platinum for temperatures up to 2000°, but it is not yet perfected.

C. E. G.

Production of Heat by Chemical Action. (Note.) By T. L. Phipson (*Compt. rend.*, lxxxvi, 1196—1197).—If a small fragment of calcium hypochlorite be held in front of a stream of sulphuretted hydrogen, the hydrogen of the latter unites so quickly with the oxygen of the former that considerable heat is evolved. The smell of the sulphuretted hydrogen is replaced by that of chlorine which is set free, and a small deposit of free sulphur takes place on the calcium hypochlorite, although the greater part of the sulphur is oxidised, forming sulphuric acid.

J. H. P.

Action of Oxygen on the Acid Chlorides and Analogous Compounds of Phosphorus and Arsenic. By Berthelot (*Compt. rend.*, lxxxvi, 859—864).—The heat of formation of metallic chlorides in the anhydrous state usually exceeds that of the corresponding oxides, so that chlorine displaces the oxygen in these oxides: on the contrary, the heat of formation of acid anhydrides by the union of oxygen with metalloids or metals exceeds that of the corresponding chlorides, so that oxygen should displace the chlorine in these oxides: in the present paper the author shows this to be true for phosphorus and arsenic. Moreover, as the heat of formation of the corresponding bromides and iodides is considerably less than that of the chlorides, the displacement of the halogen by oxygen takes place far more easily.

In fact, PCl_5 heated with oxygen in a sealed tube at 500°, yields oxychloride of phosphorus, with elimination of chlorine, this action (from the known heats of formation of the phosphorus-compounds) being accompanied by a disengagement of heat $= +39\cdot7$ (calculated at the ordinary temperature); and at a red-heat PCl_3O is transformed into phosphoric anhydride, which disengages $+74\cdot1$. With PCl_3 a similar action takes place, the total disengagement of heat being 106·1. With PBr_3 the heat disengaged by its oxidation to phosphoric anhydride is 127·3, so that when the trichloride is heated in an atmosphere of oxygen (at about 200°) it takes fire and burns to the anhydride with liberation of bromine. With PI_3 it should be 155·9.

In the case of arsenic, from the known heats of formation of arsenious and arsenic anhydrides, as determined by Thomsen, and those of the halogen compounds of arsenic determined by the author, it may be shown that the conversion of AsI_3 into arsenious anhydride would disengage 48·5. So that arsenic triiodide burns in oxygen with formation of arsenious anhydride, and liberation of iodine. The bromide, $AsBr_3$, in a similar manner disengages 18·2; the chloride, $AsCl_3$, 7·9 only; and it is found that when oxygen and the vapour of the trichloride are passed through a red-hot tube, an oxychloride is formed, but the action is incomplete, a part of the chloride escaping decomposition.

The inverse reaction is also possible, for Weber (*Pogg. Ann.*, cxii,

619) has found that $5AsO_3 + 3Cl_2 = 3AsO_5 + 2AsCl_3 (O = 8)$. This would be accompanied by a disengagement of heat = +81·4.

C. E. G.

Heat Produced by the Union of Metallic Chlorides with Ammonia. By ISAMBERT (*Compt. rend.*, lxxxvi, 968—970).—With the hope of ascertaining some relation between the heat-phenomena resulting from the combination of metallic chlorides with ammonia, and the facility with which the latter undergo dissociation, experiments were made in the first place to determine the amount of heat evolved in the union of ammonia with chlorides of silver, zinc, and calcium, a known weight of the compound being decomposed with dilute hydrochloric acid in a calorimeter. Silver chloride forms two compounds with ammonia, $AgCl.3NH_3$ and $2AgCl.3NH_3$. The former gave 10·54 heat-units, and the latter 11·58 units, calculated for one molecule of ammonia; but since the compound $AgCl.3NH_3$ is decomposed at 20° with formation of $2AgCl.3NH_3$, the former may be regarded as resulting from the union of $2AgCl.3NH_3$ with $3NH_3$, in which case it would evolve only 9·5 heat-units.

The three zinc compounds, for each equivalent of ammonia, gave respectively: $ZnCl_2.2NH_3$, 22·08 units; $ZnCl_2.4NH_3$, 16·99 units; $ZnCl_2.6NH_3$, 14·98 units; from which may be calculated $ZnCl_2.2NH_3 + 2NH_3 = 11·9$; $ZnCl_2.4NH_3 + 2NH_3 = 18·96$ units.

Calcium chloride also forms three compounds with ammonia, one molecule combining with two, four, and eight molecules of ammonia respectively. Of these, the first disengaged 14·03 units; the second, 12·16 units; and the third, 11·03 units, from which may be calculated, as before, $CaCl_2.2NH_3 + 2NH_3 = 10·29$; $CaCl_2.4NH_3 + 4NH_3 = 9·9$ units for one molecule of ammonia.

The heat of combination, therefore, appears to increase in the same ratio as the temperature required to produce with the substance the same tension of dissociation.

Since the heat evolved in the formation of $ZnCl_2.6NH_3$, 44·94 units, exceeds that disengaged in the formation of NH_4Cl (42·5), it follows that zinc chloride should retain ammonia at a temperature at which sal-ammoniac begins to dissociate; or, in other words, that between hydrochloric acid, zinc chloride, and ammonia there would be produced certain phenomena of equilibrium dependent upon the temperature and coefficients of dissociation. In order to prove this assumption, the author tried the action of anhydrous zinc chloride in fusion on sal-ammoniac, and found it to result, as he had expected, in an abundant evolution of hydrochloric acid.

J. W.

Atomic Volume and Specific Gravity of Organic Compounds. By R. HERMANN (*J. pr. Chem.* [2], xvii, 289—306).—The author's other papers on this subject appeared in abstract in this Journal, 1876, vol. ii, p. 496; and this vol., p. 637. The method of stating results in the present abstract is the same as that therein adopted.

The steric formulæ of the principal normal primary monohydric alcohols have already been given.

In *isoprimary monohydric alcohols* of the methane series the carbon atoms are to be regarded as isolated, the oxygen being united with the group $\frac{C}{0{\cdot}5}\frac{H_2}{1}$, and not with the methane atom, as in the normal primary alcohols.

The following formulæ are given:—

Propane series, $\frac{C}{1}\frac{H_4}{1} - \left(\frac{C}{0{\cdot}5}\frac{H_2}{1}\right)^{\alpha} - \left(\frac{C}{0{\cdot}5}\frac{H_2}{1}\right)^{\beta}$.

Butane " $\frac{C}{1}\frac{H_4}{1} - \left(\frac{C}{0{\cdot}5}\frac{H_2}{1}\right)^{\alpha} - \left(\frac{C}{0{\cdot}5}\frac{H_2}{1}\right)^{\beta} - \left(\frac{C}{0{\cdot}5}\frac{H_2}{1}\right)^{\gamma}$.

&c., &c.

Different isomeric alcohols are formed according as $\frac{O}{1{\cdot}5}$ is united with the group α, β, or γ.

The *secondary monohydric alcohols* are formed by hydrogenation of the ketones, $\frac{C}{1}\frac{O}{2}$ becoming condensed to $\frac{C}{1}\frac{O}{0{\cdot}5}$, and combining with $\frac{H_2}{1}$, the combinations of the hydrocarbon radicle at the same time condensing to 0·5; thus dimethyl ketone, $\frac{C}{1}\frac{H_3}{1} - \frac{C}{1}\frac{O}{2} - \frac{C}{1}\frac{H_3}{1}$ yields $\frac{C}{0{\cdot}5}\frac{H_3}{1} - \frac{C}{1}\frac{O}{1{\cdot}5}\frac{H_2}{1} - \frac{C}{0{\cdot}5}\frac{H_3}{1}$.

The secondary alcohols are converted into ketones by loss of two hydrogen-atoms in the group $\frac{C}{1}\frac{O}{0{\cdot}5}\frac{H_2}{1}$ and simultaneous expansion of the volume of the carbon atoms from $\frac{C}{0{\cdot}5}$ to $\frac{C}{1}$.

The following table represents the constitution of the more important secondary alcohols:—

		Atomic weight.	Atomic volume.	Specific gravity.		Boiling point.
				Calculated.	Observed.	
Isopropyl-alcohol	$\frac{C}{0{\cdot}5}\frac{H_3}{1} - \frac{C}{1}\frac{O}{1{\cdot}5}\frac{H_2}{1} - \frac{C}{0{\cdot}5}\frac{H_3}{1}$	60	74·5	0·805	0·791	85°
Isobutyl	$\frac{C}{0{\cdot}5}\frac{H_3}{1} - \frac{C}{1}\frac{O}{1{\cdot}5}\frac{H_2}{1} - \frac{C_2}{0{\cdot}5}\frac{H_5}{1}$	74	91·25	0·811	0·85	108·4
Isoamyl	$\frac{C}{0{\cdot}5}\frac{H_3}{1} - \frac{C}{1}\frac{O}{1{\cdot}5}\frac{H_2}{1} - \frac{C_3}{0{\cdot}5}\frac{H_7}{1}$	88	108	0·814	0·825	120
Isohexyl	$\frac{C}{0{\cdot}5}\frac{H_3}{1} - \frac{C}{1}\frac{O}{1{\cdot}5}\frac{H_2}{1} - \frac{C_4}{0{\cdot}5}\frac{H_9}{1}$	102	124·75	0·817	0·814	149

&c., &c.

Of the *tertiary alcohols*, butylic is probably $\frac{C}{1} - \frac{C}{0{\cdot}5}\frac{H_3}{1} - \frac{C}{0{\cdot}5}\frac{H_3}{1}$

$-\frac{C}{0{\cdot}5}\frac{H_3}{1}-\frac{H}{1}\frac{O}{1{\cdot}5}$; and amylic $\frac{C}{1}-\frac{C}{0{\cdot}5}\frac{H_3}{1}-\frac{C}{0{\cdot}5}\frac{H_3}{1}-\frac{C^2}{0{\cdot}5}\frac{H_5}{1}-\frac{H}{1}\frac{O}{1{\cdot}5}$.

The *dihydric alcohols*, as was pointed out in the author's first paper, differ from the monohydric alcohols by containing $\frac{O}{0{\cdot}5}$ in place of $\frac{O}{1{\cdot}5}$. A table of the principal glycols will be found on p. 499 of vol. ii for 1876. The *oxyacids* derived from the dihydric alcohols are regarded as containing oxygen with a larger atomic volume than that contained in the parent alcohol, while the volume of the carbon remains unchanged; thus the production of oxyacetic acid from ethylene glycol is formulated $\left(\frac{C_2}{0{\cdot}75}\frac{H_6}{1}\frac{O_2}{0{\cdot}5}\right)_2+2O-4H=\frac{C_4}{0{\cdot}75}\frac{H_2}{1}\frac{O_5}{2}+\frac{H_2}{1}\frac{O}{1}$.

The steric formulæ of the following members of the oxyacid series are thus tabulated:

Oxyacetic acid, $\frac{C_4}{0{\cdot}75}\frac{H_6}{1}\frac{O_5}{2}+\frac{H_2}{1}\frac{O}{1}$.

Oxypropionic acid, $\frac{C_6}{0{\cdot}66}\frac{H_{10}}{1}\frac{O_5}{2}+\frac{H_2}{1}\frac{O}{1}$.

Oxybutyric acid, $\frac{C_8}{0{\cdot}625}\frac{H_{14}}{1}\frac{O_5}{2}+\frac{H_2}{1}\frac{O}{1}$.

Oxyvaleric acid, $\frac{C_{10}}{0{\cdot}60}\frac{H_{18}}{1}\frac{O_5}{2}+\frac{H_2}{1}\frac{O}{1}$.

Oxycaproic acid, $\frac{C_{12}}{3{\cdot}583}\frac{H_{22}}{1}\frac{O_5}{2}+\frac{H_2}{2}\frac{O}{1}$.

By replacing the water of constitution of these acids by alcoholic radicles or basic oxides, ethers and salts are produced.

Thus ethylic oxyacetate has a specific gravity of 1·03, while the number calculated from the formula $\frac{C_4}{0{\cdot}75}\frac{H_3}{1}\frac{O_5}{2}\left(\frac{C_2}{0{\cdot}75}\frac{H_5}{1}\right)_2\frac{O}{2}$ is 1·00.

The steric formula of the *trihydric alcohol* glycerin has been already given. (See former abstract.)

The corresponding ether is formulated $\left(\frac{C_3}{0{\cdot}66}\frac{H_5}{1}\right)_2\frac{O_3}{2}$.

The specific gravity of *nitroglycerin* is 1·6; from the formula, $\left(\frac{C_3}{0{\cdot}66}\frac{H_5}{1}\right)_2\frac{O_3}{2}-\left(\frac{N_2}{1}\frac{O_5}{1{\cdot}5}\right)_3$, the number 1·609 is deduced.

The following hexatomic alcohols are formulated:—

Mannite, $\frac{C_6}{0{\cdot}583}\frac{H_{14}}{1}\frac{O_6}{0{\cdot}5}$.

Lævulose (glucose), $\frac{C_6}{0{\cdot}583}\frac{H_{12}}{1}\frac{O_6}{0{\cdot}5}$.

Cane-sugar, $\frac{C_{12}}{0{\cdot}583}\frac{H_{22}}{1}\frac{O_{11}}{0{\cdot}33}$.

Specific gravity = 1·6, calculated 1·613; atomic volume = 213·2, calculated = 211·97.

The conversion of two molecules of glucose into one of cane-sugar consists in the separation of one molecule of water and the condensation of $\frac{O}{0{\cdot}5}$ to $\frac{O}{0{\cdot}33}$.

The author deduces the following general conclusions from his researches upon atomic volumes and specific gravities:—

1. Chemical elements consist not only of ponderable matter possessed of different qualities, but also of an imponderable substance occupying space which, when in a state of rest, may be called latent heat.

2. The amount of latent heat associated with an elementary atom may be varied, and variation in the atomic volume may be thus brought about without alteration in the atomic weight; this is the phenomena of allotropy.

3. Such alterations in the volume of the atoms frequently accompany chemical combinations. The greater the affinity between the combining elements the greater the amount of condensation; this is shown in the following formulæ:—

A.—Compounds of Oxygen.

α. With alkali-metals $\frac{K_2}{0{\cdot}33}\frac{O}{O}$, $\frac{Na_2}{0{\cdot}33}\frac{O}{1}$, $\frac{Am_2}{0{\cdot}66}\frac{O}{1}$.

β. With alkaline earth metals $\frac{Mg}{0{\cdot}5}\frac{O}{1}$, $\frac{Ca}{0{\cdot}5}\frac{O}{1}$, $\frac{Sr}{0{\cdot}5}\frac{O}{1}$, $\frac{Ba}{0{\cdot}5}\frac{O}{1}$.

γ. With aluminum, $\frac{Al_2}{0{\cdot}5}\frac{O_3}{1}$.

δ. With earth-metals, $\frac{R}{0{\cdot}66}\frac{O}{1}$.

ε. With heavy metals, $\frac{R}{1}\frac{O}{1}$.

ζ. With silver, $\frac{Ag_2}{1}\frac{O}{1{\cdot}5}$.

B.—Haloid Compounds.

	F.	Cl.	Br.	I.
With alkali-metals....		$\frac{K}{0{\cdot}5}\frac{Cl}{0{\cdot}66}$	$\frac{K}{0{\cdot}5}\frac{Br}{1}$	$\frac{K}{0{\cdot}5}\frac{K}{1{\cdot}25}$
	Na F 0·5 0·33	$\frac{Na}{0{\cdot}5}\frac{Cl}{0{\cdot}66}$		
	—	$\frac{Am}{0{\cdot}5}\frac{Cl}{0{\cdot}66}$		

	F.	Cl.	Br.
With alkaline earth metals	$\frac{\mathrm{Ca}}{0{\cdot}5}\,\frac{\mathrm{F_2}}{0{\cdot}5}$	$\frac{\mathrm{Ca}}{0{\cdot}5}\,\frac{\mathrm{Cl_2}}{0{\cdot}66}$	$\frac{\mathrm{Ca}}{0{\cdot}5}\,\frac{\mathrm{Br}}{1}$
	—	$\frac{\mathrm{Sr}}{0{\cdot}5}\,\frac{\mathrm{Cl_2}}{0{\cdot}66}$	$\frac{\mathrm{Sr}}{0{\cdot}5}\,\frac{\mathrm{Br_2}}{1}$
	—	—	$\frac{\mathrm{Ba}}{0{\cdot}5}\,\frac{\mathrm{Br_2}}{1}$
With iron metals ...	—	$\frac{\mathrm{Ni}}{1}\,\frac{\mathrm{Cl_2}}{0{\cdot}875}$	
	—	$\frac{\mathrm{Fe}}{1}\,\frac{\mathrm{Cl_2}}{0{\cdot}875}$	—
	—	$\frac{\mathrm{Mn}}{1}\,\frac{\mathrm{Cl_2}}{0{\cdot}875}$	—
With lead metals ...	—	$\frac{\mathrm{Zn}}{1}\,\frac{\mathrm{Cl_2}}{0{\cdot}875}$	$\frac{\mathrm{Zn}}{1}\,\frac{\mathrm{Br_2}}{1}$
	—	$\frac{\mathrm{Cd}}{1}\,\frac{\mathrm{Cl_2}}{0{\cdot}75}$	$\frac{\mathrm{Cd}}{1}\,\frac{\mathrm{Br_2}}{1}$
	—	$\frac{\mathrm{Pb}}{1}\,\frac{\mathrm{Cl_2}}{0{\cdot}66}$	$\frac{\mathrm{Pb}}{1}\,\frac{\mathrm{Br_2}}{0{\cdot}75}$
With silver..........	$\frac{\mathrm{Ag}}{1}\,\frac{\mathrm{F}}{1}$	$\frac{\mathrm{Ag}}{1}\,\frac{\mathrm{Cl}}{0{\cdot}66}$	$\frac{\mathrm{Ag}}{1}\,\frac{\mathrm{Br}}{0{\cdot}75}$

C. OXYSALTS.

The oxygen-atoms of acids are the more condensed, the greater the affinity between the acids and bases:—

SO_3.	SeO_3.	CrO_3.	WoO_3.	MoO_3.
$\frac{\mathrm{K_2}}{0{\cdot}33}\,\frac{\mathrm{O}}{1}-\frac{\mathrm{S}}{1}\,\frac{\mathrm{O_3}}{1}$	$\frac{\mathrm{K_2}}{0{\cdot}33}\,\frac{\mathrm{O}}{1}-\frac{\mathrm{Se}}{1}\,\frac{\mathrm{O_3}}{1{\cdot}5}$	$\frac{\mathrm{K_2}}{0{\cdot}33}\,\frac{\mathrm{O}}{1}-\frac{\mathrm{Cr}}{1}\,\frac{\mathrm{O_3}}{2}$	—	—
$\frac{\mathrm{Ba}}{0{\cdot}5}\,\frac{\mathrm{O}}{1}-\frac{\mathrm{S}}{1}\,\frac{\mathrm{O_3}}{0{\cdot}5}$	$\frac{\mathrm{Ba}}{0{\cdot}5}\,\frac{\mathrm{O}}{1}-\frac{\mathrm{Se}}{1}\,\frac{\mathrm{O_3}}{1}$	$\frac{\mathrm{Ba}}{0{\cdot}5}\,\frac{\mathrm{O}}{1}-\frac{\mathrm{Cr}}{1}\,\frac{\mathrm{O_3}}{1{\cdot}5}$	—	—
$\frac{\mathrm{Pb}}{1}\,\frac{\mathrm{O}}{1}-\frac{\mathrm{S}}{1}\,\frac{\mathrm{O_3}}{0{\cdot}66}$	$\frac{\mathrm{Pb}}{1}\,\frac{\mathrm{O}}{1}-\frac{\mathrm{Se}}{1}\,\frac{\mathrm{O_3}}{1}$	$\frac{\mathrm{Pb}}{1}\,\frac{\mathrm{O}}{1}-\frac{\mathrm{Cr}}{1}\,\frac{\mathrm{O_3}}{1{\cdot}5}$	$\frac{\mathrm{Pb}}{1}\,\frac{\mathrm{O}}{1}-\frac{\mathrm{Wo}}{1}\,\frac{\mathrm{O_3}}{1{\cdot}5}$	$\frac{\mathrm{Pb}}{1}\,\frac{\mathrm{O}}{1}-\frac{\mathrm{Mo}}{1}\,\frac{\mathrm{O_3}}{1{\cdot}5}$

4. The evolution of heat and light during chemical combination is to be traced to condensation in the volumes of the atoms.

5. The atomic volumes of isomerides (simple and compound) are either equal, or form homologous series with equal differences.

6. The crystalline forms of elements and compounds are intimately related to their atomic volumes. For example, the polymorphism of isomeric bodies is a consequence of differences in the atomic volumes, thus:—

A.—POLYMORPHISM OF ELEMENTS.

1. *Carbon.*—Diamond, $\frac{\mathrm{C}}{0{\cdot}44}$, monometric. Graphite, $\frac{\mathrm{C}}{0{\cdot}66}$, hexagonal. Charcoal, $\frac{\mathrm{C}}{1}$, amorphous.

2. *Sulphur and Selenium.*—$\frac{\mathrm{S}}{1}$, rhombic. $\frac{\mathrm{S}}{1{\cdot}08}$, monoclinic. $\frac{\mathrm{Se}}{1{\cdot}08}$, monoclinic. $\frac{\mathrm{Se}}{1{\cdot}25}$, amorphous.

3. *Phosphorus.*—$\frac{\mathrm{P}}{1}$, rhombohedral. $\frac{\mathrm{P}}{1{\cdot}25}$, monometric. $\frac{\mathrm{P}}{1{\cdot}125}$, amorphous.

B.—POLYMORPHISM OF OXIDES.

Rutile, $\frac{\mathrm{Ti}}{1}\,\frac{\mathrm{O_2}}{0{\cdot}25}$, dimetric, P 84° 40′.

Tin ore, $\frac{\mathrm{Sn}}{1}\,\frac{\mathrm{O_2}}{0{\cdot}5}$. ,, ,,

Brookite, $\frac{\mathrm{Ti}}{1}\,\frac{\mathrm{O_2}}{0{\cdot}583}$, rhombic.

Stannic oxide, $\frac{\mathrm{Sn}}{1}\,\frac{\mathrm{O_2}}{0{\cdot}583}$, rhombic.

Anatase, $\frac{\mathrm{Ti}}{1}\,\frac{\mathrm{O_2}}{0{\cdot}66}$, dimetric, P 136° 36′.

C.—POLYMORPHISM OF CALCIUM CARBONATE.

Calcspar, $\frac{\mathrm{Ca}}{0{\cdot}5}\,\frac{\mathrm{O}}{1}\,\frac{\mathrm{C}}{1}\,\frac{\mathrm{O_2}}{1{\cdot}25}$, rhombohedral.

Aragonite, $\frac{\mathrm{Ca}}{0{\cdot}5}\,\frac{\mathrm{O}}{1}\,\frac{\mathrm{C}}{1}\,\frac{\mathrm{O_2}}{1}$, rhombic.

7. The atomic volume of nitrogen varies much; hence the great differences in the properties of nitrogen-compounds containing nitrogen in different allotropic forms.

Cyanogen, $\frac{\mathrm{C}}{1}\,\frac{\mathrm{N}}{3}$, and Prussic acid, $\frac{\mathrm{H}}{1}\,\frac{\mathrm{C}}{1}\,\frac{\mathrm{N}}{3}$, are powerful poisons; while bodies, such as proteïn-compounds, containing $\frac{\mathrm{N}}{0{\cdot}33}$ are usually most important nutritive materials.

8. Light, electricity, and magnetism, are modifications of the latent heat contained in the elements. Light is heat in a state of increased motion; electricity and magnetism are polarised heat.

M. M. P. M.

Researches on the Law of Avogadro and Ampère. By A. WURTZ (*Compt. rend.*, lxxxvi, 1170—1175).—The author has already shown that crystallised potassium oxalate does not lose its water even at a temperature above that of dissociation, if the atmosphere contains vapour of water at a greater tension than that of dissociation of the potassium oxalate. This vapour may be either free or present in chloral hydrate.

The present paper contains an account of some experiments which show inversely that dry potassium oxalate takes up water if the tension of the water vapour in the atmosphere be greater than that of dissociation at the same temperature. He has compared an atmosphere of chloral hydrate with one of damp air containing the same amount of water vapour, and with one of damp chloroform, also with the same amount of water present, at temperatures of 100° and 79°. In both cases the potassium oxalate absorbs water from the chloral hydrate atmosphere, at approximately the same rate as from the atmosphere in which the water vapour is free. From this he concludes that the vapour of water in chloral hydrate must be entirely dissociated at the temperatures at which the experiments were made. J. H. P.

Inorganic Chemistry.

Atmospheric Ozone. By A. Levy (*Compt. rend.*, lxxxvi, 1263—1265).—The author's results agree with those of Daremberg. The ozone was estimated by means of potassium arsenite, and not by ozonoscopic paper, which is affected by other elements present in the atmosphere.

Whilst papers were not coloured at Paris, to the south, at Montseuris, they were coloured blue, becoming decolorised again when the wind blew from the north, that is, from over Paris. The relation between the quantity of ozone and the direction of the wind appears to be governed by the law enunciated by Marié-Davy:—" When the centre of a storm crosses France, all the stations to the south of the trajectory show much ozone, those to the north little or none.

A relation also exists between the pressure and hygrometric state of the atmosphere, and the amount of ozone present. L. T. O'S.

Atmospheric Hydrogen Peroxide. By E. Schöne (*Deut. Chem. Ges. Ber.*, xi, 874—877).—Dew and hoar-frost formed during the later portion of the night do not contain hydrogen peroxide. Ice contains 0·05 mgms. of hydrogen peroxide per litre. The author concludes from his numerous experiments that the quantity of hydrogen peroxide in rain, hail, dew, snow, hoar-frost, &c., increases with the distance from the earth's surface at which the condensation of the aqueous vapour takes place. W. C. W.

Atmospheric Hydrogen Peroxide. By E. Schöne (*Deut. Chem. Ges. Ber.*, xi, 1028—1031).—The author considers it possible that hydrogen peroxide plays an important part in nature, *e.g.*, in destroying noxious decomposing organic matter, although it occurs only in very minute quantities in the atmosphere, the maximum amount observed being 1·4 c.c. H_2O_2 per litre of air. Numerous experiments tend to show that the amount of hydrogen peroxide in the atmosphere increases with the height of the sun above the horizon, and it is also probable that the air grows richer in hydrogen peroxide, as we approach the equator. W. C. W.

Formation of Quartz in the Dry Way. (Note.) By P. HAUTEFEUILLE (*Compt. rend.*, lxxxvi, 1194—1196).—The author has previously shown that sodium tungstate is a mineralising agent of silica, producing from it tridymite. He now shows that it will also produce quartz from amorphous silica and tridymite. For this purpose silica and fused sodium tungstate are alternately heated and cooled between the temperatures 800° and 950°. When heated, the silica combines with the soda, but on cooling it is precipitated by the tungstic acid, at first as tridymite, but below 850° as quartz. The amorphous silica disappears after several hours of alternate heating and cooling, being replaced by thin plates of tridymite, amongst which are very small crystals of quartz. The number and size of the latter increase considerably if the action of the fused salt be long continued.

The crystals have the density and polyhedric forms characteristic of quartz. With different methods of preparation the forms are found to be different. J. H. P.

Maximum Density of a Mixture of Sulphuric Acid and Water. By F. KOHLRAUSCH (*Ann. Phys. Chem. Ergänzungs-band*, viii, 675).—

Percentage H_2SO_4	100	99	98	97	96	95
Specific gravity..	1·8342	1·8376	1·8386	1·8383	1·8372	1·8352

R. R.

Alloys of Aluminium and Gallium. By L. DE BOISBAUDRAN (*Compt. rend.*, lxxxvi, 1204—1241).—The alloy obtained when excess of aluminium is heated with gallium to a dull red heat remains quite brilliant, and does not oxidise readily during its preparation. It decomposes water at the ordinary temperature, but more readily at 40°, with formation of a brown powder, which subsequently becomes changed into white flakes of alumina, almost the whole of gallium is liberated, and appears to be free from aluminium. The slow evolution of hydrogen from the solid alloy, is increased by contact with a globule of liquid gallium, an electric couple being formed.

Aluminium and gallium also form liquid and pasty alloys, which oxidise slightly in the air, but decompose water readily. The liquid alloy, when touched with a piece of solid gallium, crystallises in a manner similar to metallic gallium, but it then no longer readily decomposes water. L. T. O'S.

Atomic Weight of Glucinum. By B. BRAUNER (*Deut. Chem. Ges. Ber.*, xi, 872—874).—Nilson and Pettersson conclude from their determination of the specific heat of glucinum for temperatures between 0° and 100° that the atomic weight of this metal is 13·8, and not 9·2. In this case glucinum will form an exception to Mendelejeff's periodic law, hence the author considers it possible that the specific heat of this element may increase with the temperature. Nilson's investigations of the platinum double salts of the rarer metals are also in favour of the atomic weight Be = 9·2 rather than 13·8. The atomic weight can be definitely settled only by determining the vapour-density of the chloride, or of some other volatile glucinum compound. W. C. W.

Metallic Arsenides. By A. Descamps (*Compt. rend.*, lxxxvi, 1022—1023, and 1065—1066).—Some metals do not form definite compounds with arsenic, but alloys which lose arsenic on heating. The arsenides can be prepared by heating the metal with arsenic under a layer of fused boric acid, or by fusing an arsenate with potassium cyanide. Attempts to reduce the arsenates by the action of hydrogen or carbon monoxide at a high temperature did not yield satisfactory results. The arsenides of silver, gold, and copper may also be obtained by immersing metallic arsenic in solutions of the salts of these metals.

Silver arsenide, AgAs, is obtained in the form of a white, brittle, very hard, crystalline metallic button, sp. gr. 8·51, when silver arsenate is gently fused with potassium cyanide. It loses arsenic on heating, forming a new compound having the sp. gr. 9·01; fused under a layer of boric acid at a higher temperature, it is converted into Ag_3As, sp. gr. 9·51.

Gold arsenide, Au_3As, is deposited in the form of a dark red powder when metallic arsenic is placed in a solution of chloride of gold. By fusion with potassium cyanide, a yellow metallic button of Au_4As_3 (sp. gr. 16·2) is obtained.

Copper Arsenide, Cu_3As_2, is formed by the reduction of copper arsenate by potassium cyanide at a low temperature, or by the action of arseniuretted hydrogen on copper sulphate. It is a bluish-grey, crystalline, friable metallic body, having a sp. gr. of 6·94. Metallic arsenic throws down from a solution of copper sulphate a black precipitate of arsenide, but no metallic copper is formed. This arsenide becomes crystalline on fusion, and has the composition Cu_4As_2, sp. gr. 7·76.

By the direct union of copper and arsenic under a layer of boric acid, the brittle compound Cu_3As is obtained. It has a sp. gr. 7·81, and oxidises on exposure to the air. Heated with boric acid, this arsenide loses arsenic, and forms the steel-grey, brittle, and crystalline compound Cu_6As.

The *arsenides of lead* readily oxidise on exposure to the air, and should therefore be preserved in water or in a hydrocarbon. PbAs (sp. gr. 9·55) is obtained by the reduction of the arsenate. Pb_3As_4 formed by the direct union of lead and arsenic, has a sp. gr. of 9·65. On heating this compound with boric acid it yields Pb_3As_4(? Pb_4As_3) (sp. gr. 9·76), and at a higher temperature Pb_2As.

Nickel arsenide, Ni_3As_2 (sp. gr. 7·71), obtained by the reduction of the arsenate, is a brilliant, crystalline, metallic body. On fusion with boric acid it is converted into Ni_3As, which can also be prepared by fusing together a mixture of potassium cyanide, arsenic, and oxide of nickel.

Cadmium arsenide, Cd_3As (sp. gr. 6·26), is obtained by reducing the arsenate as a white metallic button, having a faint reddish tinge.

The *arsenides of iron* are not well defined compounds. The reduction of the arsenate yields $FeAs$, and the direct union of the arsenic with iron forms Fe_3As_2. These compounds are converted by heat into Fe_3As, and finally into a steel-white brittle substance containing 16—17 per cent. of arsenic.

The following arsenides were obtained by the direct union of arsenic with the respective metals, viz.:—

Zinc arsenides, Zn_3As_2, form brilliant octohedral crystals, which are converted by heat into Zn_3As; *Bismuth arsenide*, Bi_3As_4, sp. gr. 8·45; *Antimony arsenide*, Sb_2As (sp. gr. 6·46), a crystalline body resembling antimony in colour; and *Tin arsenide*, Sn_2As_3, a crystalline, brittle body, having a sp. gr. 6·56. W. C. W.

Allotropic Modification of Copper. By P. SCHUTZENBERGER (*Compt. rend.*, lxxxvi, 1265—1267).—By the electrolysis of a solution of acetate of copper, rendered slightly basic by boiling, in which a platinum plate serves for the negative electrode, and a somewhat larger copper plate for the positive, the face of the negative electrode which is turned towards the copper plate becomes covered with an allotropic modification of copper, which is brittle, and possesses a bronze colour, whilst the opposite face receives a thinner coat of ordinary copper. The specific gravity of the allotropic copper (which, however, could not be quite accurately determined, owing to the facility with which it oxidises) is about 8·0 to 8·2, that of ordinary copper being 6·9. Exposed to the air in the moist state, it readily oxidises to cupric oxide, CuO, showing a deep blue iridescence, also in water at 50—60°, and in a solution of basic acetate of copper. On treating it with dilute nitric acid (1 to 10) pure nitrogen monoxide is evolved, the metal being covered with a dark, olive-black layer, which has not yet been investigated. It is converted into ordinary copper by heat; and in one case, when, after drying in vacuo, it was brought into the air, much heat being disengaged. No hydrogen is evolved when it is heated to 100° in a current of carbon dioxide, so that its characteristic properties cannot be attributed to occluded hydrogen. It is probable that this modification corresponds with the copper in the cupric salts.

L. T. O'S.

Platoiodonitrites. By L. F. NILSON (*Deut. Chem. Ges. Ber.*, xi, 879—885).—The platoiodonitrites are generally prepared by the action of a metallic sulphate on barium platoiodonitrite. The silver, lead, and hydroxyl-compounds are, however, precipitated from the barium salt by their respective nitrates, and the calcium and strontium platoiodonitrites are obtained from their platonitrites by the action of iodine and alcohol. The silver, lead, thallium, and hydroxyl salts are insoluble in water, the remaining salts are soluble. Most of the platoiodonitrites are very stable, and do not decompose at 100°, others, however, split up into nitrite and platinous iodide. *Potassium platoiodonitrite*, $K_2N_2O_4I_2Pt + 2H_2O$, has been previously described (*Ber.*, x, 930). The platinum in this salt is not precipitated by sulphuretted hydrogen, nor is the iodine removed by silver nitrate.

Rubidium platoiodonitrite, $Rb_2N_2O_4I_2Pt + 2H_2O$, forms large shining tabular crystals, which lose their water of crystallisation at 100°. The *cæsium* salt, $Cs_2N_2O_4I_2Pt + 2H_2O$, crystallises in small prisms, which lose their 2 mols. of water at 100°. *Ammonium platoiodonitrite*, $Am_2N_2O_4I_2Pt + 2H_2O$, large tabular crystals, which decompose slowly at 70°, but rapidly at 100° into water, nitrogen, and platinous iodide. *Thallium platoiodonitrite*, $Tl_2N_2O_4I_2Pt$, separates out as an insoluble crystalline precipitate, when sodium platoiodonitrite is added to a solution of thallium sulphate. *Sodium platoiodonitrite*, $Na_2N_2O_4I_2Pt + 4H_2O$, crystallises in large prisms, which lose their water at 100°. *Lithium platoiodonitrite*, $Li_2N_2O_4I_2Pt + 6H_2O$, forms long deliquescent prisms, which lose 5 mols. of water at 100°. The silver salt, which has been previously described (*loc. cit.*), gradually decomposes into silver iodide and a platinum compound. *Calcium platoiodonitrite*, $CaN_2O_4I_2Pt + 6H_2O$, crystallises in large prisms, which only lose one molecule of water at 100°. *Strontium platoiodonitrite*, $SrN_2O_4I_2Pt + 8H_2O$, forms large four-sided columns. It loses 6 mols. of water at 100°.

The *barium* salt has been previously described. The *lead* compound, $PbN_2O_4I_2Pt + PbO_2H_2$, is precipitated on the addition of lead nitrate to the barium salt.

Magnesium platoiodonitrite, $MgN_2O_4I_2Pt + 8H_2O$, crystallises in large four-sided tables; *manganese platoiodonitrite*, $MnN_2O_4I_2Pt + 8H_2O$, is deposited in irregular six-sided prisms, which are completely decomposed at 100°. *Nickel and cobalt platoiodonitrites* form respectively green and yellow four-sided prisms, containing 8 mols. of water, which are decomposed at 100°. The *ferrous* salt crystallises in greenish-yellow four-sided prisms, containing 8 mols. of water, and is decomposed at 100°. The *copper* salt has not been obtained in the pure state. *Zinc platoiodonitrite*, $ZnN_2O_4I_2Pt + 8H_2O$, forms four-sided prisms, which are decomposed at 100°. The *cadmium*-compound, $CdN_2O_4I_2Pt + 2H_2O$, does not change when heated to 100°.

When mercuric chloride is added to barium platoiodonitrite mercuric iodide is precipitated; mercurous nitrate produces a dark-brown precipitate, having the formula $Hg_2N_2O_4I_2Pt + Hg_2O + 9H_2O$.

Glucinum platoiodonitrite, $Be_23(N_2O_4I_2Pt) + 18H_2O$, forms small yellow crystals, which decompose at 100°. The aluminium salt contains 27 mols. of water, in other respects it resembles the preceding compound. The solution of the *chromium* salt decomposes on evaporation *in vacuo*. *Ferric platoiodonitrite*, $Fe_23(N_2O_4I_2Pt) + 6H_2O$, crystallises in greenish-yellow needles, which decompose at 100°.

Yttrium platoiodonitrite, $Y_23(N_2O_4I_2Pt) + 27H_2O$, is a yellowish-green deliquescent crystalline mass, which decomposes at 100°. The erbium and cerium salts contain 18 mols. of water; the lanthanum and didymium salts contain 24; in other respects these platoidonitrites resemble the yttrium-compound. W. C. W.

Mineralogical Chemistry.

Mineralogical Notes from the East Indian Archipelago. By A. FRENZEL (*Jahrb. f. Min.*, 1878, 80—81).—The author examined some mineral specimens collected by A. B. Meyer, of Dresden, in 1870—73, in the East Indies:—

1. *Borneo.*—In the Sarawak Kingdom in this island antimony ores and cinnabar are found, viz., at Tambusan and Tagui; *antimonite* occurs in large quantity, partly quite pure and fibrous, or massive, sometimes intermixed with quartz, and converted into *antimony-ochre* on the surface. The antimony-ochre occurs in two varieties, the one being a compound of antimonoso-antimonic oxide, calcium antimonate, and water, occurring in long fibrous aggregations, having a hardness 3. sp. gr. 2·7 to 2·8, and a straw-yellow colour; the other variety is a reddish-yellow cervantite, having a hardness 5, and sp. gr. 5·09. *Native antimony* is found at the above-mentioned localities in large tin-white, granular, laminated masses free from gold, and often weighing one pound. Together with this native antimony very fine sheaf-like *valentinite* and antimony blende are found, and in hollow spaces in the antimony a peculiar antimonial mineral occurs in small, apparently quadratic crystals (exhibiting numerous forms), possessing a strong adamantine lustre, and of a wine or greenish-yellow colour. Frenzel considers this mineral to be a new one, and proposes for it the name Sarawakite. *Native arsenic* is found in two varieties, accompanied by antimonite, quartz, and realgar; the first being the characteristic undulating shell-like variety; the second, a granular or "short lamellar" variety, which rapidly tarnishes blackish-grey; the latter is found at Gading. *Cinnabar* is found in an aluminous rock penetrating clay-slate, near Tegora and Gading, accompanied by iron pyrites, hepathic iron pyrites, and calomel (in the form P.0P).

2. *Phillippine Islands.*—*Copper ores* are found in the Island of Luzon at Mancayan, in the district of Lepanto. *Enargite* (exhibiting the same forms as that found at Morococha, in Peru) in small well-defined crystals and large rough crystals. *Luzonite* occurs massive and crystallised. The author considers luzonite to be an independent species and monosymmetrical, the forms somewhat resembling those of epidote. *Magnesia alum* is found on the Island of Negros in a volcanic region; it is the same in constitution as the African and American magnesia alum.

3. *Timor.*—Copper ores are found here in large and promising quantities. C. A. B.

Calamine rich in Indium. By A. and G. de NEGRI (*Gazzetta chimica italiana*, viii, 120).—The calamine from the mines of Onela, in the Province of Bergamo, is very rich in indium, and may be used advantageously for its preparation. C. E. G.

Iron Pyrites from Schwelm in Westphalia (*Dingl. polyt. J.*, ccxxviii, 283).—The above ore extends over a surface of 600,000 square meters, the rock having a thickness of 3 to 10 meters. It is largely used for the manufacture of sulphuric acid, the burnt ore being an excellent raw material for preparing Bessemer steel. It is free from arsenic, and contains but little phosphorus and copper. The following is the composition given by Schmidt :—

$$\underbrace{\overset{Fe_2O_3.}{90\cdot547}\quad\overset{FeO.}{\cdot520}}_{65\cdot0556\text{ p.c. Fe.}}$$

FeS.	PbS.	CuS.	MnO.	Al_2O_3.	CaO.
·574	·142	·026	·463	1·448	·388

MgO.	H_2SO_4.	H_3PO_4.	SiO_2.	H_2O.
·220	1·110	·035	3·447	·897 = 99·817 p.c.

D. B.

Tellurite. By F. A. GENTH (*Jahrb. f. Min.*, 1878, 73—74).—Tellurite was hitherto known to occur at Zalathna, in the Faczebaier Gebirge, Siebenbürgen, in small radio-fibrous globular groups, accompanied by tellurium, situated in drusy spaces on grey quartz. The author found this mineral in Colorado, in the Keystone, Smuggler, and John Jay Mines, Boulder County, occurring in hollows and fine rifts in tellurium, the crystals being sometimes isolated and sometimes grouped together in sheaves, and striated longitudinally. Cleavage distinct, parallel to one direction. Colour white to yellowish-white. Vitreous lustre, and adamantine lustre upon cleavage planes. The matrix of tellurite is quartz. C. A. B.

The Crystal Forms of Tin Stone (Cassiterite). By F. BECKE (*Jahrb. f. Min.*, 1878, 76—78).—Cassiterite from Finland is characterised by the occurrence of 0P and ∞P2, in addition to the prisms ∞P and ∞P∞. The pyramid P is also generally present, whilst at Penonta, in Gallicia, it occurs independently. P∞ is commonly observed on Bohemian cassiterite; $\frac{1}{4}$P is peculiar to the cassiterite from Pitkaranta; 3P$\frac{3}{2}$ is mostly observed on specimens from Cornwall, Bohemia, and Finland. The pyramid $\frac{7}{2}$P$\frac{7}{5}$ is new, and was observed by the author on Cornish cassiterite. There are three types of crystals, viz.:—

1. *Bohemian and Saxon Type.*—Moderately large and thick long crystals, ∞P predominating, with ∞P∞, ∞P2, P, P∞, and occasionally 3P$\frac{3}{2}$. The crystals generally occur as twins. The cassiterite of Gallicia in Spain, and Nertschinsk in Siberia, belongs to this type.

2. *English Type.*—Acicular, simple crystals and not twins are the rule. The terminals of the crystals generally exhibit the following combinations, viz: P.3P$\frac{3}{2}$, or P.P∞, or P.P∞. 3P$\frac{3}{2}$; the prisms ∞P2, ∞P$\frac{3}{2}$, are common, whilst ∞P∞ is comparatively rare. 0P is also observed occasionally. The cassiterite of Malacca, Banca, and Potosi, belongs to this type. Included in this type is the radio-fibrous, microcrystalline, acicular cassiterite, called "wood-tin," which is sometimes found in geniculated twins, which are characterised by the "knee-bend" being "attached;" a property which serves to distinguish it from the geniculated twins of Saxon cassiterite, which are characterised by free "knee-bends" and well-defined re-entering angles.

3. *Pitkaranta or Finnish Type.*—Characterised by the predominance of $0P$ and $\infty P\frac{3}{2}$. There are numerous prisms, but $\infty P2$ is completely absent. Twins exceedingly rare. Vicinal faces are often observed on P and ∞P, also sub-individuals upon the same faces. C. A. B.

Horn Mercury from el Doctor, Mexico. By WEBSKY (*Jahrb. f. Min.*, 1878, 72—73).—Burkart found this rare mineral at the mine in the above-mentioned locality (*Jahrb. f. Min.*, 1866, 411), and stated that it was described (together with the coccinite from Casas Viejas, Mexico) as chloroselenide of mercury. Websky contends that it is nothing more than an impure horn mercury. He found a specimen in the Berlin Museum occurring upon a deposit of onofrite, a circumstance which suggests that the horn mercury in this instance is a secondary product of the decomposition of onofrite. The horn mercury on all the Berlin specimens occurs on a coarse-grained limestone coloured with ferric oxide, in brown crystals 1 mm. to 2 mm. in length. Above these crystals there is a fresh siskin-green or greenish-grey mass, which passes into a confused mass of indistinct acicular crystals, and out of this large and pure horn mercury crystals project. Twenty-three forms were observed on these crystals, including six pyramids of the first order, four pyramids of the second order, and eight ditetragonal pyramids. Up to this time the horn mercury crystals of Moschellandsberg (described by Schrauf) were unrivalled, but the Mexican horn mercury equals it in interest. Websky takes as primary pyramid one having an angle of 135° 40′ measured over a terminal edge. Some crystals are flat and tabular, exhibiting the following combination, viz., $\infty P\infty.\frac{1}{4}P\infty.P\infty.\frac{1}{3}P.\frac{3}{5}P3$. They are mostly rough and rhombic in type. The majority of the crystals belong probably to a more recent formation, being smooth and shining, and exhibiting the forms $\infty P\infty.\frac{1}{3}P.\frac{1}{2}P.\infty P.$ in combination, also secondary $\frac{1}{4}P\infty$ and $P\infty$. Another form observed was $0P.3P.2P\infty$. and the new pyramid $\frac{1}{9}P$. C. A. B.

Pandermite (a Mineral discovered by Muck). By G. VOM RATH (*Jahrb. f. Min.*, 1878, 74—75).—This mineral was found at Panderma, on the Black Sea, in a grey streaky gypsum bed, lying under a formation composed of alternating layers of brown clay and calcareous slate. Pandermite is found in snow-white, fine-grained nodules and fragments, enclosed in the gypsum. An analysis of the dried mineral showed it to have the following composition, viz.:—

CaO.	MgO.	FeO.	K_2O.	H_2O.	BO_3.	
29·33	0·15	0·30	0·18	15·45	54·59	= 100·00

The author considers the formula $2CaO.3Bo_2O_3 + 3H_2O$ to be the most appropriate one for this mineral. No chlorine, sulphuric acid, silica, or carbonic acid, could be detected in it. From the above it appears that pandermite is nearly related to borocalcite. C. A. B.

Crystallised Vivianite in Bones from the Laibach Peat-bog. By F. BECKE (*Jahrb. f. Min.*, 1878, 79—80).—Vivianite was found in acicular crystals 2—3 mm. in length, and exhibiting the combination $\infty\breve{P}\infty$. $\infty\bar{P}\infty$. ∞P. P. $\bar{P}\infty$, also in tabular aggregates and sheaf-like groups; the latter occurring mostly on the exterior of the bones, whilst the well-defined crystals were in the interior. Distinct pearly lustre upon $\infty\breve{P}\infty$, the other faces were striated and dull. By reflected light the crystals appear to have a fine indigo-blue colour; by transmitted light they appear to be almost colourless, with an intensely coloured outer zone, showing that the blue colour has not penetrated very deeply. C. A. B.

Vivianite as a Petrifying Medium. By O. FRAAS (*Jahrb. f. Min.*, 1878, 80).—The author described (*Jahrb. f. Min.*, 1877, 971) some fossil remains of "Aëtosaurus ferratus," the bones of which appear to be of interest to mineralogists, as their hollow spaces are filled with clay ironstone, whilst the bones themselves are converted into vivianite, the "ground colour" of the whole being brown-red ferric oxide. These remains were found at Kaltenthal, near Stuttgart. C. A. B.

Accidental Colouring of Zeolitic Minerals. By WEBSKY (*Jahrb. f. Min.*, 1878, 75—76).—The colouring matter of zeolites may be divided into two classes, viz.: (1) a mechanical intermixture of ferric oxide, which imparts a red colour to the zeolites of Dumbarton in Scotland and the Fassa Thal in the Tyrol; (2) a coloration induced by organic compounds, such as that observed in the desmine and heulandite from the magnetic iron-ore formations of Arendal in Norway, where the asphalt occurring in that neighbourhood is the direct colouring medium. The zeolites from Gräben, west of Striegau in Silesia, are very interesting examples of the last-mentioned coloration. They occur in drusy cavities in granite, and each species has its characteristic shade of colour (which remains constant), although several species occur simultaneously on the same specimen. *Desmine* is the commonest, occurring in pale leather-brown to wood-brown coloured crystals. *Chabasite* occurs in crystals of a full chestnut-brown to orange-red colour, the colour being very intense upon the surface, and somewhat less so in the interior. This mineral appears to absorb the greatest amount of colouring matter: on heating some of it in a closed tube it blackens, and tarry matter distils off, but on cooling, the fragment has a greyish hue, unless the ignition has been prolonged, when the fragment appears white. *Heulandite* is rare in the Striegau district, and has a lemon-yellow colour. One specimen of this mineral was covered with small and perfectly colourless laumontite crystals. It is certainly remarkable that minerals having similar elementary compositions (chabasite, desmine, heulandite, laumontite) should exhibit such marked differences in their absorptive power for organic colouring matters. C. A. B.

The Mica-group. By G. TSCHERMAK (*Jahrb. f. Min.*, 1878, 71—72).—It is well known that diaxial magnesia micas exist, and that diaxial micas allow of two kinds of orientation, the uniting line between the optical axis in the first lying in a diagonal of the hexagonal lamellæ; whilst it is perpendicular to that direction in the second. Uniaxial mica was called *biotite* by Hausmann, whilst certain micas with small optical axes were called *phlogopite* by Dana. The diaxial micas were all called muscovite. Iron-free lithia-mica is called lepidolite and is similar to muscovite in its properties, but that containing iron (zinnwaldite) resembles phlogopite. The optical and crystallographical work of this investigation was very carefully carried out by Tschermak, and the chemical analyses were made by E. Ludwig, the finest and purest crystals only being selected for examination.

As the results of former investigations the author arranged the micas in the following manner:—

I.		II.	
Biotite.	Anomite.	Meroxene.	Lepidomelane.
Phlogopite.	—	Phlogopite.	Zinnwaldite.
Muscovite.	Lepidolite.	—	—
—	Muscovite.	—	—
—	Paragonite.	—	—
Margarite.	Margarite.	—	—

The micas in Class I exhibit the same optical orientation, the plane of the optical axes being perpendicular to the plane of symmetry, whilst the plane of the optical axes in the micas belonging to Class II is parallel with the plane of symmetry. Anomite is a rare mica with peculiar chemical composition. Meroxene is the name given to all vesuvian micas. Tschermak concludes that *all micas belong to the monosymmetrical system*, and that their twin-formation leads to the assumption of a system of axes which is characterised by the two axes in the plane of symmetry intersecting each other almost at an angle of 90°. This last peculiarity accounts for the rhombic types at one time and rhombohedral types at another time observed to occur in these micas. The optical relationships of the micas is given in the following table, the dispersion being stated in the usual manner, and in addition $+f$ signifies whether the positive optical axis angle is greater by an increased amount of iron in the mineral and $-f$ whether the same angle is diminished by an increase of iron:—

I.		II.	
Anomite	$\rho > v + f$.	Meroxene	$\rho < -f$.
		Phlogopite ...	$\rho < -f$.
Lepidolite	$\rho > v$.	Zinnwaldite ..	$\rho < -f$.
Muscovite	$\rho > v + f$.		
Paragonite	$\rho > v$.		
Margarite	$\rho > v$.		

From this table it appears that with micas of Class I the dispersion is generally $\rho > v$ up to margarite, and with the micas of Class II $\rho < v$ up to zinnwaldite. In all these cases no relationship was observed between the chemical and optical properties, a fact which agrees with Tschermak's observations in respect to augite and bronzite.

C. A. B.

Rose-red Anorthite from the Pesmeda Alp. By G. vom Rath (*Jahrb. f. Min.*, 1878, 78).—This is found on the south side of the Monzoni, associated with green fassaite, dark pleonast, bluish-grey calcite, specular iron, and chabasite. There are two systems of twin lamellæ, one according to the law "the twin-plane the brachypinacoid," the other exhibits a striation on the brachypinacoid, the twin-plane being parallel to the macroaxis. The red colour of this anorthite disappears on ignition, the residue being white. Loss on ignition 2·73; sp. gr. 2·689. Chemical composition:—

SiO_2.	Al_2O_3.	CaO.
42·60	34·05	18·04 = 94·69

C. A. B.

Analysis of the Leonhardite from Floitenthal. By A. Smita (*Jahrb. f. Min.*, 1878, 81—82).—The specimens described by Bezina (*Jahrb. f. Min.*, 1877, 644) were analysed by the author with the following results, viz.:—

SiO_2.	Al_2O_3.	CaO.	H_2O.
52·92	22·44	12·23	12·38 = 99·97

Sp. gr., 2·374; formula, $Si_4Al_2CaH_6O_{16}$.

Rammelsberg considers leonhardite to be a laumontite which has lost one molecule of water. Smita instituted further inquiries into the subject, and obtained the following results, viz.:—(1.) *Laumontite* contains two molecules of water of crystallisation (the formula being $Si_4Al_2CaH_8O_{18}$), one of which is given off slowly in dry air, and rapidly at 100°, whilst the second is only driven out completely at 300°. The remaining two molecules of water are driven out only at a red heat, and are water of constitution or hydroxyl-groups. (2.) *Leonhardite* is a laumontite which has lost the molecule of water given off at 100°: the chemical composition of that found in nature, however, corresponds with the formula $Si_4Al_2CaH_6O_{15}$ only after drying at 100°.

C. A. B.

Formation of the Meteoric Brecchia on St. Catherine, Brazil. By S. Meunier (*Compt. rend.*, lxxxvi, 943—946).—Of the two specimens of meteoric iron from St. Catherine, one is characterised by the presence of a considerable quantity of *millerite*, nickel sulphide mixed with pyrrhotine, while the other contains pyrrhotine only; both constitute true metallic brecchias cemented together by sulphides.

An examination of the sulphides proved so conclusively that they owed their origin to the action of sulphuretted gases on the metal of the meteorite itself, that the author was induced to attempt the artificial production of a similar consolidated brecchia by imitating the supposed mode of formation of the St. Catherine specimen. Fragments of cast-iron were placed in a crucible, and submitted for eight hours to the action of hydrogen sulphide at a red heat. After cooling, the fragments were found to be incrusted with pyrrhotine, whilst many of them were cemented together by the same substance. The formation of iron sulphide was also accompanied by an elimination of carbon, which arranged itself between the metal and the sulphide exactly in the same manner as in the natural specimen, and it further resembled the latter in that it contained occluded hydrogen and gave imperfect figure-markings on treatment with acids.

The success of these experiments has of course greatly strengthened the opinion which was expressed respecting the origin of the St. Catherine meteorite. Moreover, the type is very exactly represented among terrestrial rocks by certain specimens of brecchiform jasper, in the description of which the word jasper would be substituted for iron, quartz for sulphur, and calcite for graphite. These brecchias appear to have been originally fragments of jasper, which having been acted upon by thermal waters, became finally cemented together by deposited silica. Fine fissures, subsequently produced, traversing both the quartz and jasper have been afterwards incrusted by crystals of calcite, whilst the original interstices existing between the fragments of jasper have also been filled up by deposits of the same substance. An analogy apparently so complete between the structure of these two cosmical specimens could scarcely obtain, save by reason of similarity in their respective conditions of formation. J. W.

Mineral Spring at Marpingen, Alsweiler, Trèves. By H. VOHL (*Deut. Chem. Ges. Ber.*, xi, 878).—100,000 grams of this water contain total solids 6·6 grams; loss on ignition, 2·00. CaO 1·34; MgO 0·89; FeO 0·30; SiO_2 0·48; H_2SO_4 0·34; Cl 0·01; traces of potash, soda, and nitrous acid; carbonic acid and loss, 1·24.

W. C. W.

Composition of the Birresborn and Gerolstein Mineral Springs at Pelm, in the Eifel. By H. VOHL (*Deut. Chem. Ges. Ber.*, xi, 877).—1000 parts of water contained:—

	Gerolstein (sp. gr. 1·002875).	Birresborn (sp. gr. 1·00567).
Soda	1·2230	1·4289
Potash	0·0313	0·2817
Lithia	0·0004	0·0008
Lime	0·4869	0·1062
Magnesia	0·1334	0·3415
Alumina	0·0002	traces
Ferrous oxide	0·0348	0·0153
Manganous oxide	0·0003	0·0003
Chlorine	0·9889	0·2168
Bromine	0·0002	0·0003
Iodine	0·000002	0·000004
Sulphuric acid	0·0147	0·1005
Phosphoric acid	0·0043	0·0001
Silica	0·1194	0·0245
Baryta and strontia	0·0001	traces
Boric acid, nitric acid, and organic matter.	traces	traces.

The amount of carbonic acid in the waters was not estimated.

W. C. W.

Analysis of the Mineral Water of Casteggio. By A. and E. DE NEGRI (*Gazzetta chimica italiana*, viii, 120—121).—This water has an alkaline reaction and bitter saline taste: the depth of the well is 11 meters, and the temperature 11·5°, that of the external air being 10°. Its sp. gr. is 1·0079, and it contains total solids 12·895698 grams per litre, or 12·793351 per kilogram.

	Per litre.	
Oxygen	0·008029	= 5·6 c.c.
Nitrogen	0·026597	= 21·2 c.c.
Sodium chloride	8·997944	
Magnesium chloride	2·215240	
Calcium chloride	0·831236	
Potassium chloride	0·293422	
Ammonium chloride	0·004029	
Lithium chloride	0·002358	
Rubidium and cæsium chlorides	traces	
Magnesium bromide	0·046637	
,, iodide	0·005325	
Calcium bicarbonate	0·282857	
Magnesium carbonate	0·065480	
Ferrous ,,	0·006293	
Manganous ,,	0·000330	
Cobalt, bismuth, and zinc carbonates.	0·000379	
Ammonium nitrate	0·069779	
Calcium sulphate	0·007493	
Barium ,,	0·000353	
Strontium sulphate	0·000280	
Aluminium phosphate	0·000417	
Silica	0·031220	
Organic matter	1·218928	
Water	993·885374	

C. E. G.

Chemical Examination of the Warm Springs of Schlangenbad. By R. FRESENIUS (*J. pr. Chem.* [2], xvii, 306—320).—1. *Schachtquelle.*—Rate of flow = 28 litres per second; temperature = 31°. The carbonates are calculated as normal salts; all salts are without water of crystallisation.

Potassium sulphate	0·013860 per 1000.
Potassium chloride	0·009016
Sodium chloride	0·270489
Sodium bromide	0·000112
Sodium phosphate	0·000134
Sodium carbonate	0·001802
Lithium carbonate	0·002627
Calcium carbonate	0·038405
Strontium carbonate	0·000331
Magnesium carbonate	0·008791
Silica	0·033351
Total	0·378918

Carbonic acid combined with the carbonates to form bicarbonates....	0·023786	per 1000.	
Free carbonic acid	0·042072	,,	or 23·77 c.c. in 1000 c.c. water at the temperature of the water, and at 760 m.m.
Nitrogen	0·012320	,,	or 10·93 ,,
Oxygen	0·004101	,,	or 3·19 ,,
Total constituents....	0·461197	,,	

Traces of cæsium and rubidium chlorides, sodium iodide, borate, and nitrate, barium carbonate, and ferrous carbonate were found.

The waters of the other wells are very similar to that of the Schachtquelle. By comparing this analysis with that published by the author in 1852, it is seen that the water of the Schlangenbad wells has remained essentially unaltered during the last 26 years. Small differences are noticeable, as in the case of all mineral waters, but the water is now in all leading characters the same as it was in 1852.

M. M. P. M.

Organic Chemistry.

Formation of Hydrocarbons by the Action of Water on a Carbide of Iron and Manganese. By S. Cloez (*Compt. rend.*, lxxxvi, 1248—1251).—Neither cold nor boiling water acts on spiegeleisen, but when superheated steam is passed over the alloy, heated to dull redness, hydrogen, carbon dioxide and traces of marsh-gas are produced.

By the action of dilute sulphuric acid on a ferromanganese containing iron 56·5 per cent., and manganese 38·2 per cent., and combined carbon 5·0 per cent., large quantities of paraffins and olefines are evolved; pure water, however, acts only at temperatures above 300°.

An alloy, which gave the following numbers on analysis, Mn 85·4, Fe 5·7, Si 1·2, combined carbon 3·7, graphitic carbon 4·0, was readily attacked by water yielding hydrogen, and gaseous and liquid hydrocarbons.

A similar alloy, containing 81·5 per cent. manganese, when acted on by water at 100°, yielded liquid hydrocarbons and a gas which contained hydrogen mixed with some olefines, the products being similar to those formed by the action of dilute acid on cast iron.

From these experiments it follows that when warm water is decomposed by a carbide of manganese and iron, part of the hydrogen set free is evolved as such, and the remainder combines with the carbon to form hydrocarbons, the metals being oxidised to protoxides.

L. T. O'S.

Isomeric Amylenes. By A. WISCHNEGRADSKY (*Compt. rend.*, lxxxvi, 973—974).—In a paper by A. Étard on the preparation of amylene (this vol., 392), it is stated that the amylene obtained, boiling at 35—38°, and furnishing a hydriodide boiling at 125°, is isopropylethylene. The object of the present communication is to show that such could not be the case, but that, on the contrary, it was trimethylethylene.

The author's experiments have confirmed the statement of Flavitzky, that ordinary amylene prepared by means of zinc chloride consists mainly of trimethyl-ethylene, mixed with about 10 per cent. of an isomeric hydrocarbon, which yields methylpropyl-carbinol on hydration; and Eltékoff has since proved that small proportions of methylethyl-ethylene and isopropyl-ethylene are generally present. Ordinary amylene is then a mixture of several isomerides, of which the boiling points vary between 22 and 40°. But tertiary amyl alcohol (dimethylethyl-carbinol), which is easily obtained from commercial amylene, furnishes pure trimethyl-ethylene of constant boiling point 36°, and a hydriodide boiling at 127—128°.

The olefine prepared by the action of alcoholic potash on fermentation amyl iodide, is a mixture of two isomerides; one of which is isopropyl-ethylene, boiling at 21·5°, and insoluble in sulphuric acid. Its hydriodide boils at 137—139°.

It is obvious, therefore, that the amylene of Étard which boiled at 35—38° is no other than trimethyl-ethylene, and not isopropyl-ethylene, as he imagined. Moreover, the former hydrocarbon is the one which is most largely produced by the action of zinc chloride on fermentation amyl alcohol, the unsymmetrical methyl-ethyl-ethylene being formed at the expense of the active alcohol. Trimethyl-ethylene is not very soluble in sulphuric acid, unless the mixture is well agitated and its temperature maintained at 0°. J. W.

Hexine from Mannite. By O. HECHT (*Deut. Chem. Ges. Ber.*, xi, 1050—1055).—Hexine, C_6H_{10}, is obtained by heating monobromohexylene (derived from mannite hexylene) with alcoholic potash in sealed tubes, at 170° for 12 hours; about $\frac{1}{3}$ of the bromide remains undecomposed. The hydrocarbon is a colourless mobile liquid, possessing a pungent, disagreeable odour. It is optically inactive, and its sp. gr. is 0·7494 at 0°, and 0·7377 at 13°, referred to water at 0°. Hexine remains liquid at − 20°, and boils between 80 and 83°; it is miscible in all proportions with alcohol, ether, chloroform, carbon bisulphide, benzene, light petroleum, and glacial acetic acid, and it dissolves in sulphuric acid, sp. gr. 1·83. It does not produce a precipitate in ammoniacal solutions of silver or cuprous salts. As the hydrocarbon yields carbonic, acetic, and normal butyric acids on boiling with chromic acid solution, its constitutional formula is probably $CH_3.C{\equiv}C.CH_2.CH_2.CH_3$.

Hexine dibromide, $C_6H_{10}Br_2$, produced by the direct union of bromine and hexine, is an optically inactive liquid, of a pale-yellow colour. It does not solidify at − 20°, and it begins to decompose at 130°. The sp. gr. of the liquid is 1·6977 at 0°, and 1·5543 at 100°. Bromine acts slowly on hexine dibromide, hydrobromic acid is evolved, and a heavy yellow oil (sp. gr. 2·1625 at 0°) is formed, which thickens to a syrup at − 15°, and begins to decompose at 160°. It is probably a mixture of $C_6H_{10}Br_4$ and $C_6H_9Br_3$. W. C. W.

Action of Chlorine on Ethyl Bromide. By H. Lescœur (*Bull. Soc. Chim.* [2], xxix, 483—485).—By the action of chlorine on ethyl bromide in diffused daylight, hydrogen is replaced by chlorine without liberation of bromine, several isomerides being formed.

(1.) The first body is, when pure, a colourless liquid, having a sp. gr. 1·07 at 30°, and boiling at 84·5° under a pressure of 765 mm., it does not solidify at −19°. On exposure to light it acquires a yellow colour, and evolves acid vapours. It is insoluble in water, but soluble in alcohol and ether, and has an odour resembling that of chloroform. The analyses and vapour density correspond with the formula C_2H_4ClBr. By the action of silver oxide it yields aldehyde, and treating it with silver acetate a liquid is obtained which boils between 160 and 166°, and reduces ammoniacal silver solutions. It is, therefore, ethylidene chlorobromide. Its boiling point, 84·5°, is the mean between those of ethylidene dichloride (60°) and dibromide (110°).

(2.) The second body, an isomeride of the first, is a colourless liquid, which decomposes in the sunlight, and has a sp. gr. = 1·79 at 0°. It boils at 104—108°, and is insoluble in water, but soluble in alcohol and ether. Alcoholic potash acts on it violently with formation of chlorethylene, C_2H_3Cl; by the action of silver acetate, glycol diacetate is formed, $C_2H_4(C_2H_3O_4)_2$. It is, therefore, ethylene chlorobromide, the boiling point of which is intermediate between that of ethylene dichloride (85°), and ethylene dibromide (137°). These two bodies form the chief product of the reaction.

Two other isomerides, boiling respectively at 137 and 151°, are also formed, the analyses and vapour densities of which correspond with the formula $C_2H_3Cl_2Br$.

The last product of the reaction is a liquid boiling between 158—162°, sp. gr. at 0° = 2·113. The analysis and vapour density, which are, however, not satisfactory, agree best with the formula $C_2H_3Cl_2Br$.

The chemical properties of the three last bodies require further investigation. L. T. O'S.

Methylenemethylamine. By J. Romeny (*Deut. Chem. Ges. Ber.*, xi, 835—837).—A mixture of hexmethyleneamine and methylenemethylamine, C_2H_5N, is obtained by passing trimethylamine in a current of hydrogen through a red hot tube. The following reactions are supposed to take place:—

(1.) $N(CH_3)_3 = NCH_3(CH_2) + CH_4$.
(2.) $NCH_3.(CH_2) = HCN + CH_4$.
(3.) $N(CH_3)_3 + H_2 = NH(CH_3)_2 + CH_4$.
(4.) $NH(CH_3)_2 + H_2 = NH_2.CH_3 + CH_4$.
(5.) $NH_2.CH_3 + H_2 = NH_3 + CH_4$.

When methylenemethylamine is boiled with dilute hydrochloric acid, it splits up into methaldehyde and methylamine:—

$$C_2H_5N + H_2O = H_2CO + H_2NCH_3.$$

W. C. W.

Action of Iodine on Guanidine Carbonate and on Nitroso-Guanidine. By V. RECHENBERG (*Deut. Chem. Ges. Ber.*, xi, 870—872).—By the action of iodine on guanidine carbonate, and on nitrosoguanidine under different conditions, several crystalline compounds were obtained, which, however, have not yet been analysed.

W. C. W.

Polymerisation of Ethylene Oxide. Note by A. WURTZ (*Compt. rend.*, lxxxvi, 1176).—The author has made a number of experiments to determine the conditions under which ethylene oxide is converted into the polymeride which he has previously described. If a very small fragment of recently fused potash, or, still better, fused zinc chloride be added to the liquid, the whole will become a solid mass of the polymeride after the lapse of a few months. Fused calcium chloride does not polymerise the ethylene oxide, but merely turns it brown and decomposes it.

A trace of hydrochloric acid, or of ethylene chloride, will not effect the polymerisation. J. H. P.

Action of various Substances on Crystallisable Sugar. By H. PELLET (*Ann. Chim. Phys.* [5], xiii, 394).—The author has made numerous experiments on the quantity of glucose formed by the influence of heat, time, and various substances on sugar, and comes to the following conclusions:—

(1.) Under the influence of heat and time, weak sugar-solutions alter more rapidly than concentrated solutions.

(2.) Glucose assists in the transformation of sugar into glucose, in proportion to the pre-existing quantity, but its action becomes *nil* when the sugar-solution is saturated (Gunning).

(3.) Mineral salts act strongly on sugar at a certain temperature. Chloride of potassium appears to be more energetic in its action than the nitrate. Ammonium nitrate has a very energetic action. By boiling for 30 minutes a mixture of 100 c.c. of water, 10 grams of sugar, and 5 grams ammonium nitrate, all the sugar is transformed into glucose.

(4.) Organic salts have a very weak action.

(5.) The quantity of glucose found in the molasses from the refinery is determined by the total influence of time, heat, and mineral salts, in addition to the quantity of glucose pre-existing in the unrefined sugar. C. W. W.

Dissociation of Chloral Hydrate. By MOITESSIER and R. ENGEL (*Compt. rend.*, lxxxvi, 971—973).—If chloral hydrate dissociates on heating, it is probable that the tension of its vapour at the boiling point is greater than the atmospheric pressure acting upon it at that moment. In order to test the truth of this hypothesis, and to determine the tension of its vapour, quantities of chloral hydrate, varying from 0·015 to 2·0 grams, were enclosed in the sealed limb of a small Mariotte's tube of 15 mm. diameter, and the whole heated in calcium chloride bath to nearly the boiling point of the hydrate. The level of the mercury in the open limb, although previously a little lower than that in the closed limb, quickly ascended until it stood considerably higher than the level in the closed limb, notwithstanding that the temperature of the bath was below the boiling point of the hydrate. The observed tensions of vapour were as follows:—

95·8° = 769·5 mm. 97·3° = 814·5 mm.
96·5° = 789·5 „ 97·5° = 817·9 „

Different specimens of chloral gave similar results.

The authors confirm the statement of Cannizzaro that the temperature of the *vapour* of boiling chloral hydrate is lower than that of the boiling *liquid*, the former being about 97 to 97·5°, whilst the latter is 105°.

They consider that the results are quite conclusive respecting the dissociation of this substance, since it appears impossible to explain, otherwise than by dissociation, the fact that the tension of its vapour at the boiling point is greater than the atmospheric pressure.

J. W.

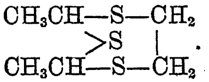
Thialdehydes. By H. KLINGER (*Deut. Chem. Ges. Ber.*, xi, 1023—1027).—The author considers that the α-acethialdehyde, described by Weidenbusch (*Annalen*, lxvi, 158), is not a pure compound, since the crude product of the action of sulphuretted hydrogen on an acid aqueous solution of aldehyde can be separated by treatment with alcohol into two substances, one of which is easily soluble, and the other but sparingly soluble. The latter is deposited from a dilute solution in alcohol or glacial acetic acid in long colourless prisms, which melt at 101°. This substance boils without decomposition at 246—247°, and its vapour-density is 6·27, corresponding with the formula $C_6H_{12}S_3$. A better method of preparing α-acethialdehyde is to pass sulphuretted hydrogen through liquid thialdehyde suspended in water; the oily liquid which separates out, and which has the composition $8CH_3CHS.H_2S$, and a specific gravity of 1·127 at 25°, can be kept over strong hydrochloric acid without undergoing polymerisation. The oil dissolves in hot alcoholic hydrochloric acid, and separates out again on cooling. On the addition of a few drops of aldehyde it rapidly polymerises, forming α-acethialdehyde. When water is added to a solution of the oil in strong sulphuric acid, sulphur dioxide is evolved, and sulphur and β-acethialdehyde separate out.

The β modification, which the author previously obtained by the action of acid chlorides on the liquid thialdehyde (*Ber.*, ix, 1893, and x, 1877), and which is also formed by the action of acetyl chloride on the α-acethialdehyde, melts at 124—125°, and boils at 245—248°. The vapour-density of this body, 6·27, shows that it is an isomeride of the acethialdehyde melting at 101°.

α-Thialdehyde forms two compounds with silver nitrate, viz., $(CH_3.CHS)_3AgNO_3$, and $(CH_3.CHS)_33AgNO_3$, which do not deposit silver sulphide on boiling with alcohol. The crystalline compounds which mercuric chloride, platinum chloride, and silver nitrate form with α-thialdehyde, are easily distinguished from the corresponding β salts.

The two isomerides yield the same products on oxidation with dilute nitric acid, viz., aldehyde, sulphur, acetic, carbonic, oxalic, and sulphuric acids.

One of them probably has the constitution:—



$$\begin{array}{l} CH_3CH{-}S{-}CH_2 \\ \qquad\;\; >S \quad | \\ CH_3CH{-}S{-}CH_2 \end{array}.$$

W. C. W.

Solubility of Organic Acids in Alcohol and Ether. By E. BOURGOIN (*Bull. Soc. Chim.* [2], xxix, 242—247).—The author's results were obtained volumetrically by titrating saturated solutions with standard baryta-water. The quantity of acid dissolved by 100 parts by weight of each solvent is given in the following table:—

Acid.	Ether.	Absolute alcohol at 15°.	Alcohol of 90°.
Oxalic	1·266	23·73	14·70
Succinic	1·265	7·51	12·59
Tartaric	0·4	25·604	41·135
Citric	2·26	75·90	52·85
Gallic	2·56	38·79	23·31
Benzoic	31·35	46·68	41·62
Salicylic	50·47	49·63	42·09
Phthalic	0·684	10·08	11·70

F. J. L.

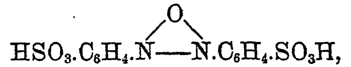
Action of Potassium Cyanide on Dichloracetic Ether. By A. CLAUS (*Deut. Chem. Ges. Ber.*, xi, 1043—1044).—Dichloracetic acid and potassium dichloracetate are decomposed by continued boiling with an alcoholic solution of potassium cyanide, forming oxalic and acetic acids. Malonic acid is not found to be one of the products of decomposition of dichloracetic acid, and glycollic acid is obtained only when potassium cyanide is used which contains free alkali.

W. C. W.

Monobromopyromucic Acid. By R. SCHIFF and G. TASSINARI (*Deut. Chem. Ges. Ber.*, xi, 842).—An addition product, $C_5H_4O_3.Br_2$, is formed by adding bromine to a solution of ethyl pyromucate in glacial acetic acid: this is decomposed by treatment with alcoholic potash, forming potassium monobromopyromucate, and the potassium salt of a new acid, having the formula $C_4HO.COOH$, which has not, however, been obtained in a state of purity. Monobromopyromucic acid, $C_4H_2BrO.COOH$, crystallises in colourless needles, which melt at 155° C., and readily sublime. W. C. W.

A New Method of Synthesis of the Hydrocarbons. By F. LANDOLPH (*Compt. rend.*, lxxxvi, 1267—1270).—By the action of fluoborethylene on camphor at 200° the elements of water are eliminated, and a hydrocarbon is obtained which boils between 185—190°. It has an odour slightly resembling that of camphor, and from its analysis and vapour density has the formula $C_{12}H_{18}$. Its constitution however, may be either ethyl-cymene, $C_6H_3(C_2H_5)(CH_3)(C_3H_7)$, or ethylene-cymene, $C_6H_4(CH_3).C_2H_4.C_3H_7$, but its constitution and products of oxidation require further study.

By treating other bodies with fluorborides, different hydrocarbons may be obtained. L. T. O'S.

Azoxy- Azo- and Hydrazo-Compounds. By H. LIMPRICHT (*Deut. Chem. Ges. Ber.*, xi. 1044—1049).—*Meta-azoxybenzene-sulphonic acid*,  $HSO_3.C_6H_4.N\overset{O}{—}N.C_6H_4.SO_3H$, obtained by the action of sulphuric acid on its barium salt, crystallises in small yellow needles, soluble in water and in alcohol. Its salts have a yellow colour. *Potassium meta-azoxybenzene-sulphonate*, $C_{12}H_8.N_2O.(SO_3K)_2 + 4H_2O$, is prepared by evaporating to dryness a mixture of alcoholic potash and potassium metanitrobenzene-sulphonate, and heating the residue at 120°. The crude product is dissolved in a small quantity of water and allowed to evaporate slowly, when soluble needle-shaped crystals are deposited. The *ammonium salt* forms rhombic prisms containing 2½ molecules of water of crystallisation, and the *barium salt* crystallises in small rhombic prisms containing 1 molecule of water, which are sparingly soluble in water. The *calcium salt* crystallises with 3½, and the *lead salt* with 1 molecule of water, in sparingly soluble needles. The action of phosphorus pentachloride on potassium meta-azoxybenzene-sulphonate gives rise to the chloride, $C_{12}H_8.N_2O.(SO_2Cl)_2$, which is deposited from its solution in toluene in yellowish-red rhombic prisms (m. p. 138°).

Meta-azobenzene-sulphonic acid, $HSO_3.C_6H_4.N{=}N.C_6H_4.SO_3H + 3H_2O$, prepared from the barium salt, crystallises in pale-yellow monoclinic prisms terminating in pyramids. It is sparingly soluble in water and in alcohol, and its salts have a yellow or red colour. The *potassium salt* is obtained in yellow needle-shaped crystals by adding zinc-dust to a hot mixture of potassium hydrate and nitrobenzene sulphonate. *Sodium meta-azobenzene-sulphonate*, $C_{12}H_8N_2(SO_3Na)_2 3\frac{1}{2}H_2O$, forms very soluble monoclinic prisms; the *ammonium salt* crystallises in dark-red monoclinic tables containing 2 mols. of water, the *barium salt* occurs in very soluble tabular crystals containing 5 mols. of water, and the *lead salt* forms short prisms containing 4½ mols. of water.

The *chloride*, $C_{12}H_8N_2(SO_2Cl)_2$, is deposited from an ethereal solution in ruby-red needles, which melt at 166—167°. The *amide*, $C_{12}H_8N_2(SO_2NH_2)_2$, produced by the action of ammonia on the preceding compound, forms yellow needles sparingly soluble in water and in alcohol. It melts above 260°.

Hydroazobenzene sulphonic acid, $HSO_3.C_6H_4.(NH)_2.C_6H_4.SO_3H + 3\frac{1}{2}H_2O$, is produced by the action of zinc-dust or ferrous sulphate on an alkaline solution of azobenzene-sulphonic acid, or by treating azoxybenzene-sulphonic acid with stannous chloride, but the simplest method of preparation is to warm sodium azobenzene-sulphonate with an acid solution of stannous chloride, dissolve the precipitate which is thrown down in caustic soda, filter, and acidify with hydrochloric acid. The hydrazobenzene-sulphonic acid which separates out is dissolved in hot water, from which it is deposited in colourless monoclinic prisms, sparingly soluble in water and in alcohol. This acid is not attacked by reducing agents. The *potassium salt*, $C_{12}H_8(NH)_2(SO_3K)_2 + 1\frac{1}{2}H_2O$, forms colourless, soluble, monoclinic prisms, the *barium salt* crystallises in tables containing 4 mols. of water, and the *lead salt*, which forms pale-red sparingly soluble rhombic crystals, also contains 4 mols. of water.

When hydrazobenzene-sulphonic acid is heated with water to 200°, it splits up into sulphuric acid and a new monosulphonic acid, $C_{12}H_9(NH)_2SO_3H + 2\frac{1}{2}H_2O$, which forms yellow needle-shaped crystals soluble in water and in alcohol. The *potassium and barium salts* contain 4 mols. of water and crystallise in yellow scales, which dissolve readily in water. The *lead salt*, $(C_{12}H_9(NH)_2SO_3)_2Pb + 3H_2O$, occurs in very soluble red needles. The *chloride*, $C_{12}H_9(NH)_2SO_2Cl$, is deposited from an ethereal solution in yellow scales (m. p. above 240°).

Azoxy- azo- and hydrazo-benzenesulphonic acids are decomposed by nitrous acid, crystalline compounds being formed. W. C. W.

Attempts to Prepare Alums containing Aniline and Rosaniline. By W. H. WOOD (*Chem. News*, xxxviii, 1).—In view of the similarity of constitution between ammonia, methylamine, aniline, and rosaniline, it was thought probable, as the first two of these easily form alum, that aniline and rosaniline might also form alums, at least with alumina. Various attempts were therefore made, both with commercial and with pure materials, but in no case was there the slightest indication of the formation of an alum, the constituent materials always crystallising out with but small portions of impurity.

It was not thought necessary to make any attempt to prepare analogous compounds containing iron, chromium, or manganese in place of aluminium, since these alums are all less stable than ordinary alum.

C. W. W.

A Base, $C_{19}H_{18}N_2$. By C. BÖTTINGER (*Deut. Chem. Ges. Ber.*, xi, 840—842).—When a solution of benzylene chloride in alcoholic ammonia is heated in sealed tubes at 100°, ammonium chloride and benzaldehyde are formed. The same change takes place at the ordinary temperature if a small quantity of zinc-dust is added to the mixture.

The base $C_{19}H_{18}N_2$ previously obtained by the author (p. 506) by the action of aniline on benzylene chloride was not a pure compound. The base forms a crystalline compound with benzene, sparingly soluble in the latter, and when heated with mercuric chloride at 100°, it yields a substance which dissolves in alcohol, forming a reddish-blue solution, which dyes silk blue. Benzylene chloride also acts on orthotoluidine and dimethylaniline, forming bases which have not yet been obtained in a state of purity. Paratoluidine is only attacked by benzylene chloride at a high temperature, a yellow solid body being the product of the reaction. W. C. W.

Action of Water on Phosphenyl Chloride; a Phenylated Solid Phosphoretted Hydrogen, $C_6H_5P_4H$. By H. GÖTTER and A. MICHAELIS (*Deut. Chem. Ges. Ber.*, xi, 885—888).—Phosphenylous acid is formed when phosphenyl chloride is acted on by excess of water, but if water is added to phosphenyl chloride (in the proportion of their molecular weights) at a temperature of 100°, and the mixture is afterwards heated to 260°, hydrochloric acid is evolved and a yellow substance is formed, from which water and alcohol dissolve out phosphenylic, phosphenylous, and phosphoric acids, leaving a residue soluble in carbon bisulphide. On evaporating the carbon bisulphide solution, yellow flakes of phenylated phosphoretted hydrogen, $C_6H_5P_4H$, separate out, leaving in the mother-liquor a compound which is very soluble in carbon bisulphide. *Phenylated phosphoretted hydrogen* is also formed by exposing phosphenyl chloride to moist air. It is a dark-yellow amorphous powder, insoluble in water, alcohol, ether, and cold carbon bisulphide. It dissolves in nitric acid, forming phosphenylous, phosphenylic, and phosphoric acids.

The compound soluble in carbon bisulphide has the composition $C_6H_5P_4H + C_6H_5PO_2$. It is a yellow powder, insoluble in water, alcohol, and ether; it dissolves in nitric acid forming phosphenylic and phosphoric acids. *Di-phenylphosphinic acid*, $(C_6H_5)_2PO_2H$, best prepared by the action of water on phosphenyl chloride, forms large triclinic crystals which lose half a molecule of water at 230°. The calcium salt, $Ca\{(C_6H_5)_2PO_2\}_2 + 3H_2O$, is more soluble in cold than in hot water. *Ethyl diphenylphosphinate* forms colourless needles (m. p. 165°). The products of the action of phosphenylous acid on phosphenyl chloride are identical with those obtained by the action of 1 molecule of water on 1 molecule of phosphenyl chloride.

W. C. W.

Oxidation of Xylenesulphonic Acids. By M. W. ILES and I. REMSEN (*Deut. Chem. Ges. Ber.*, xi, 888—892).—The authors find that the sulphamine-metatoluic acid, which they obtained by oxidising a mixture of isomeric xylene-sulphamides, is derived from the amide melting at 137°, and not from that melting at 95—96°. The constitution of this acid may be represented by the formula

$$C_6H_3(CH_3)(COOH)NH_2SO_2(1:3:6),$$

since it forms xylidic acid, $C_6H_3(CH_3)(COOH).COOH(1:3:6)$, on fusion with sodium formate. By fusing sulphamine-metatoluic acid with potash, an oxytoluic acid, $C_6H_3.CH_3.COOH.OH(1:3:6)$, is obtained, which splits up into carbon dioxide and orthocresol when heated to 180° in sealed tubes with strong hydrochloric acid, or on heating with quicklime. This acid is an isomeride of that which Jacobsen prepared (*Ber.*, xi, 374) by fusing xylenol with potash.

W. C. W.

Monobromo-α-Metaxylene-sulphonic Acid. By E. WEINBERG (*Deut. Chem. Ges. Ber.*, xi, 1062—1064).—On the addition of water to a solution of monobromometaxylene, $C_6H_3(CH_3)(CH_3)Br(1:3:6)$ (b. p. 205—208°), in cold fuming sulphuric acid, a crystalline deposit is obtained of *monobromo-α-metaxylenesulphonic acid*,

$$C_6H_2(CH_3)(CH_3)(SO_3H)Br + 2H_2O(1:3:4:6),$$

which, after repeated crystallisation from dilute sulphuric acid, forms colourless scales or prisms, soluble in water and in dilute alcohol. Attempts to prepare this acid by brominating a cold aqueous solution of α-metaxylenesulphonic acid or sodium metaxylenesulphonate, did not yield good results, but *barium monobromo-α-metaxylenesulphonate*, $[C_6H_2Br.(CH_3)_2SO_3]_2Ba + H_2O$, can be easily obtained in the form of crystalline scales by slowly adding bromine to a cold solution of barium α-metaxylenesulphonate ($C_6H_3.CH_3.CH_3.SO_3H$ (1 : 3 : 4). The following salts were prepared;—$C_6H_2Br(CH_3)_2.SO_3Na + H_2O$, small needles, readily soluble in water; $C_6H_2Br(CH_3)_2.SO_3NH_4 + H_2O$, long silky needles, very soluble in water; $[C_6H_2Br(CH_3)_2SO_3]_2Zn + 9H_2O$, long rhombic prisms; $[C_6H_2Br(CH_3)_2SO_3]_2Cu + 7H_2O$, easily soluble greenish-white scales. By the action of phosphorus pentachloride on the anhydrous sodium salt the acid chloride, $C_6H_2Br(CH_3)_2SO_2Cl$, is obtained. This substance forms large transparent crystals (m. p. 61°) which are sparingly soluble in alcohol but insoluble in water.

Monobromo-α-metaxylenesulphamide, $C_6H_2Br(CH_3)_2.SO_2NH_2$, prepared by the action of ammonia on the preceding compound, is deposited from an alcoholic solution in rhombic prisms (m. p. 194°) and from a hot aqueous solution as a crystalline powder. W. C. W.

Compounds of Picramide. By K. H. MERTENS (*Deut. Chem. Ges. Ber.*, xi, 843—846).—A solution of picramide in benzene, when slowly evaporated, deposits pale yellow transparent prisms which fall to pieces on exposure to the air. The formula for this compound is $C_6(NO_2)_3H_2.NH_2.C_6H_6$. Toluene forms a similar compound, which crystallises in brown transparent needles. A solution of picryl chloride in benzene deposits large pale yellow transparent prisms containing equal numbers of molecules of the two constituents.

Crystalline compounds separate out when warm concentrated alcoholic solutions of aromatic bases are added in excess to picramide. At 100° the base contained in these bodies is volatilised. *Picramide aniline*, $C_6(NO_2)_3H_2NH_2.C_6H_7N$, forms black shining prisms or needles; *picramide paratoluidine* and *dimethylaniline* also form black shining crystals. Phenylpicramide or picrylaniline does not form compounds with hydrocarbons or with bases. Dipicrylamine (m. p. 234°) prepared by pouring a solution of diphenylamine in strong sulphuric acid into fuming nitric acid, does not unite with bases, but combines with 2 molecules of naphthalene. The beautiful yellow transparent prisms thus formed are permanent in the air, but lose their naphthalene completely at 100°. W. C. W.

Action of Bromine on Phenoldisulphonic Acid. By M. v. SCHMIDT (*Deut. Chem. Ges. Ber.*, xi, 852—858).—When a concentrated aqueous solution of potassium phenoldisulphonate is added to bromine (1 mol. of the salt to 1 of bromine), small yellow crystals of potassium dibromophenolmonosulphonate, $C_6H_3Br_2KSO_4$, separate out as the mixture cools. On evaporating the mother-liquor, a white salt crystallising in rhombic plates is obtained. This substance is very soluble in water, but insoluble in alcohol. It gives with ferric chloride a deep ruby-red coloration which is destroyed by the addition of sodium carbonate. The free acid, $C_6H_5BrS_2O_7$, prepared in the usual way from the lead salt, forms a dark crystalline deliquescent mass which is readily soluble in water and alcohol. Nitric acid converts this body into picric acid. The potassium salt, $C_6H_3BrK_2S_2O_7$, produces in a solution of barium chloride a colourless crystalline precipitate of *barium monobromophenoldisulphonate*, $C_6H_3BrBaS_2O_7 + 2H_2O$, and with lead acetate it forms $C_6H_3BrPbS_2O_7$. It is not precipitated by solutions of cobalt, chromium, nickel, uranium, copper, mercury, gold, or calcium. Silver nitrate does not give an immediate precipitate with the potassium salt unless the mixture is boiled. Potassium bromophenoldisulphonate is completely oxidised by fusion with potash.

Tribromophenol is formed when excess of bromine acts on potassium phenoldisulphonate. W. C. W.

Action of Sulphuryl Chloride on Resorcin and on Ethylene Glycol. By G. REINHARD (*J. pr. Chem.* [2], xvii, 321—346).—By adding an equivalent amount of sulphuryl chloride, drop by drop, to resorcin dissolved in absolute ether, and distilling, *monochlororesorcin*, $C_6H_3Cl(OH)_2$, was obtained, as a white crystalline body, melting at 89°, but beginning to sublime at 75°, and distilling at 255—256°. Monochlororesorcin is soluble in water, alcohol, ether, benzene, and carbon bisulphide: its aqueous solution slightly reddens litmus paper. It is attacked by warm dilute nitric acid, with evolution of chlorine and nitrous acid, and formation of a hard resinous mass. With ferric chloride it forms a blue-violet colour, becoming brown on heating. Ammoniacal silver solution is reduced by monochlororesorcin. It seems to form a very unstable potassium derivative, $C_6H_3Cl(OK)_2$. No derivatives could be obtained by fusing with potassium hydrate or cyanide: the action of bromine upon an aqueous solution of the substance at 80° results in the formation of *monochlordibromoresorcin*, $C_6HBr_2Cl(OH)_2$, which crystallises in slender brilliant needles, melting at 105°. The *benzoyl derivative*, $C_6H_3Cl(OC_7H_5O)_2$, is produced by the action of benzoyl chloride upon monochlororesorcin: it crystallises from hot alcohol in small hexagonal needles, melting at 98°, and, when saponified, yields a benzoate and the original monochlororesorcin.

Dichlororesorcin is obtained by rubbing together in a basin resorcin and sulphuryl chloride, in the proportion of 1 to 2 molecules, heating after addition of a very little more sulphuryl chloride, and subliming two or three times. Dichlororesorcin is very soluble in water and other ordinary solvents: by evaporation of its aqueous solution over sulphuric acid, it is obtained in well-formed rhombic prisms, readily efflorescing in air, melting at 77°, and boiling at 249°. *Dichloromonobromoresorcin*, $C_6H_3BrCl_2O_2$, is obtained by the action of bromine upon dichlororesorcin, and the *benzoyl derivative*, $C_6H_2Cl_2(OC_7H_5O)_2$, by the action of benzoyl chloride: the former melts at 100°, the latter at 127°.

Sulphuryl oxychloride acts energetically on dichlororesorcin, with formation of a white solid, consisting of microscopic rhombic crystals, soluble in potash and in potassium carbonate solution (in the latter case with evolution of carbon dioxide), but insoluble in water, alcohol, and ether. This substance has the empirical formula, $C_{12}H_6Cl_4S_2O_9$, and the probable structural formula,

$$C_6HCl_2(OH)_2SO_2—O—SO_2(OH)_2Cl_2HC_6.$$

By decomposing a solution of this body in potassium carbonate with hydrochloric acid, evaporating on the water-bath, and crystallising from alcohol, the free acid, $C_6HCl_2(SO_3H)(OH)_2$, was obtained as a white powder, soluble in water and in alcohol, and decomposed by sulphuryl oxychloride into the anhydride and water. The insoluble barium salt was obtained by boiling the anhydride with baryta-water, or by precipitating a solution of the anhydride in potassium carbonate with barium chloride. By gradually adding to resorcin about six times its own weight of sulphuryl chloride, heating for some hours in a flask fitted with a reversed condenser, distilling off excess of sulphuryl chloride, drying *in vacuo* over potash, and repeatedly crystallising from hot water, *trichlororesorcin*, $C_6H_3Cl_3O_2$, was obtained in the form of small brilliant needles, readily soluble in alcohol and in ether, melting at 83°, but subliming only with partial decomposition.

By treating an aqueous solution of resorcin with excess of chlorine, trichlororesorcin was obtained, melting at 73°. The author regards this body as identical with that obtained by the action of excess of sulphuryl chloride upon resorcin; the difference between the melting points he attributes to small amounts of impurities.

Trichlororesorcin forms a *benzoyl derivative*, $C_6HCl_3(OC_7H_5O)_2$, which melts at 133°. Sulphuryl chloride, heated with trichlororesorcin in a sealed tube, reacts upon the latter body at 160°. The tetrachlororesorcin probably produced has not yet been obtained in the pure state.

Sulphuryl chloride exerts an energetic action upon ethylene glycol, which may be thus formulated:—

$$C_2H_4(OH)_2 + SO_2Cl_2 = C_2H_4(OH)(OSO_2Cl) + HCl.$$

The new body could not be obtained in a state of perfect purity. It forms a heavy colourless oil, quickly becoming brown in the air, soluble in ether, and decomposed by water, with production of glycol, sulphuric acid, and hydrochloric acid.

A very unstable potassium salt, $C_2H_4(OH)(OSO_3K)$, was obtained by the action of a warm solution of potassium carbonate upon $C_2H_4(OH)(OSO_2Cl)$. M. M. P. M.

Dimethylresorcin Derivatives. By M. Hönig (*Deut. Chem. Ges. Ber.*, xi, 1039—1042).—By passing chlorine through a mixture of glacial acetic acid and dimethylresorcin until the solution has a dark violet colour, monochlorodimethylresorcin is formed; but if the action of the chlorine is continued until the dark colour disappears and the liquid turns a pale yellow, the dichloro-derivative is obtained.

Monochlorodimethyl-resorcin, $C_8H_9ClO_2$, forms long needle-shaped transparent crystals (m. p. 118°), which are insoluble in cold glacial acetic acid, and in cold alcohol, but are soluble in ether and in boiling alcohol. *Dichlorodimethylresorcin* is a yellow oily liquid, insoluble in water, sparingly soluble in alcohol, and easily soluble in ether and in glacial acetic acid. It decomposes at 140°.

When bromine is added to a mixture of glacial acetic acid and dimethylresorcin, transparent rhombic crystals of *dibromodimethylresorcin* separate out. This substance melts at 137—138°, and dissolves sparingly in alcohol and glacial acetic acid, but easily in ether.

Nitro-derivatives.—The mononitrodimethylresorcin could not be prepared. The dinitro-compound, $C_8H_8(NO_2)_2O_2$, is obtained by adding to a mixture of dimethylresorcin and glacial acetic acid, an equal volume of strong nitric acid, and extracting with ether. The residue left on evaporating the ethereal solution, after being purified by crystallisation from hot dilute alcohol, forms reddish-brown crystals (m. p. 67°), soluble in ether and alcohol, but insoluble in water. To prepare *trinitrodimethylresorcin*, $C_8H_7(NO_2)_3O_2$, a mixture of equal volumes of strong nitric acid and dimethylresorcin is poured into cold concentrated sulphuric acid; the addition of water causes the substance to separate out in the form of crystalline scales (m. p. 123—124°), which dissolve in ether and alcohol, but are insoluble in water. W. C. W.

Dimethylhydroquinone Derivatives. By J. HABERMANN (*Deut. Chem. Ges. Ber.*, xi, 1034—1039).—A solution of dimethylhydroquinone in glacial acetic acid readily absorbs chlorine, and deposits colourless needle-shaped crystals (m. p. 126°) of *dichlorodimethylhydroquinone.* This substance is soluble in ether, alcohol, and hot glacial acetic acid, but does not dissolve in water. On saturating the mother-liquor from the dichloro-dimethylhydroquinone with chlorine, yellowish-white needles of tetrachloro-dimethylhydroquinone, $C_6Cl_4O_2(CH_3)_2$, separate out, which melt at 153—154°, but begin to sublime at a lower temperature. It dissolves easily in alcohol and glacial acetic acid. The filtrate from the tetrachloro-dimethylquinone contains chloranil and another chlorinated compound, which sublimes in violet crystals (m. p. 79°), and is very soluble in alcohol.

Dibromo-dimethylhydroquinone, prepared by slowly adding bromine to a solution of dimethylhydroquinone in hot glacial acetic acid, forms colourless crystals, which melt at 142°, and sublime without decomposition. It is soluble in boiling glacial acetic acid, and insoluble in water.

Mononitro-dimethylhydroquinone separates out in the form of golden crystals, when strong nitric acid is added to an emulsion of dimethylhydroquinone and warm water. The substance melts at 70—71°, sublimes at higher temperatures, and dissolves in alcohol.

Dinitro-dimethylhydroquinone is obtained by adding to a solution of dimethylhydroquinone in glacial acetic acid an equal volume of strong nitric acid. After the mixture has been allowed to stand for 15 minutes; water is added, which precipitates the substance in the form of a yellow crystalline powder. It is soluble in alcohol and glacial acetic acid, but is insoluble in water. It melts at 169—170°, and sublimes readily.

Trinitro-dimethylhydroquinone is formed on adding a solution of dimethylhydroquinone or of dinitro-dimethylhydroquinone in glacial acetic acid, to a well-cooled mixture of sulphuric and fuming nitric acid. On dilution with water, a yellow precipitate is produced, which dissolves in hot alcohol, and is deposited from the alcoholic solution in yellow brittle prisms. W. C. W.

Substituted Benzaldehydes. By C. L. JACKSON and J. H. WHITE (*Deut. Chem. Ges. Ber.*, xi, 1042—1043). — *Parachlorobenzaldehyde*, $C_6H_4Cl.COH$, is prepared by boiling pure parachlorobenzyl bromide (from paratoluidine) with lead nitrate and water, in an atmosphere of carbonic anhydride for three days, and then distilling the mixture. On adding hydrogen-sodium sulphite to the distillate, a crystalline sparingly-soluble precipitate is formed, which, when treated with sodium carbonate, yields the pure aldehyde. All these operations must be conducted in a current of carbonic anhydride. Parachlorobenzaldehyde is not liquid at the ordinary temperature, as stated by Beilstein and Kuhlberg (*Annalen*, cxlvii, 352), but forms white scales, which melt at 47·5°, and dissolve in ether, benzene, alcohol, carbon bisulphide, glacial acetic acid, and in boiling water. The aldehyde is rapidly oxidised by potassium permanganate, and slowly by the oxygen of the air to parachlorobenzoic acid (m. p. 233—234°).

Parabromobenzaldehyde (m. p. 57°) and para-iodobenzaldehyde (m. p. 73°) resemble the preceding aldehyde in their chemical properties.

W. C. W.

Sulphoparabromobenzoic Acid. By C. BÖTTINGER (*Liebig's Annalen*, cxci, 13—29).—The sulphoparabromobenzoic acid,

$$C_6H_3Br.(SO_3.CO_2).H_2,$$

was prepared by heating concentrated sulphuric acid and pure parabromobenzoic acid at 120—130° for eight hours, and, after cooling, pouring the mixture into a large quantity of cold water. The filtered solution is neutralised with barium carbonate, filtered, and the barium salt obtained in the crystalline state by evaporation. After purification of the barium salt by recrystallisation, the acid may be liberated by decomposing it with sulphuric acid. When pure, the new acid crystallises in colourless needles, and occasionally in large transparent prisms, very easily soluble in water, and forms two classes of salts, neutral and acid.

Barium sulphoparabromobenzoate, $C_6H_3Br(SO_3.CO_2)Ba + 3H_2O$, is readily soluble in hot water, but only soluble with difficulty in cold water, from which it separates in large transparent crystals. When a hot concentrated solution is treated with hydrochloric acid, long needles of the acid salt $\{C_6H_3Br(SO_3.CO_2)\}_2BaH_2$, separate out on cooling. The neutral *potassium* and *sodium* salts are colourless needles, very easily soluble in water. The acid *sodium* salt, $C_6H_3Br(SO_3.CO_2)NaH$, is very readily soluble in water, and easily soluble in alcohol, from which it crystallises in long needles containing 2 molecules of water. The *silver* salt, $C_6H_3Br(SO_3.CO_2)Ag_2 + 3Aq$, consists of hard crystals, soluble with great difficulty in water. The calcium, zinc, and magnesium salts crystallise in needles, and are all soluble in water. The *copper* salt, $C_6H_3Br(SO_3.CO_2)Cu + 3Aq$, crystallises in splendid groups of blue needles, readily soluble in water. The *lead* salt, $C_6H_3Br(SO_3.CO_2)Pb + 7Aq$, crystallises in very fine groups of radiating needles, which dissolve with difficulty in water.

Sulphoparabromobenzoic chloride was prepared by acting on dry powdered sodium sulphoparabromobenzoate with phosphoric chloride, in the molecular proportion of 1 to 4. The action gradually becomes energetic, and must be moderated by cooling. When it is complete, the mass is gradually added in small portions to a large quantity of water: a heavy oil separates, which, after careful washing, gradually solidifies to a hard white mass of the crude chloride. The crude chloride, when dried, is treated with anhydrous ether, which separates it into two portions; a monochloride, which remains behind as a snow-white mass, and a dichloride, which readily dissolves, and crystallises out as a yellowish mass, melting at a low temperature to a dark oily liquid.

Sulphoparabromobenzoic monochloride, $C_6H_3Br(SO_2Cl).COOH$, crystallises from ether in long snow-white needles, melting at 197°, with partial decomposition. It is soluble with great difficulty in water and alcohol, somewhat more easily in cold ether, and is moderately soluble in hot ether.

Ethyl sulphoparabromobenzoate, $C_6H_3Br(SO_2OC_2H_5).COOH$, crystallises in lustrous plates, melting at 84°, and is prepared by acting on the monochloride with alcohol, hydrochloric acid being eliminated.

Amidosulphoparabromobenzoic acid, $C_6H_3Br(SO_2NH_2).COOH$, prepared by the action of alcoholic ammonia on the monochloride, crystallises in nodules composed of small white needles, melting at 229—230°, soluble with difficulty in cold water, easily in boiling water. It dissolves with great facility in aqueous ammonia, forming an ammonium salt, $C_6H_3Br(SO_2NH_2).CO_2NH_4$, a body which loses ammonia on evaporation. When the amido-acid is dissolved in warm baryta water, small hard glittering needles separate out, consisting of the barium salt.

Ethyl sulphoparabromobenzamate, $C_6H_3Br(SO_2OC_2H_5).CONH_2$, is formed at the same time as the amido-acid by the action of alcoholic ammonia on the dichloride contained in the crude monochloride. As it is but sparingly soluble in alcohol and almost insoluble in water, it is easily separated from the acid. It crystallises in long colourless needles, which melt at 128°, and are readily soluble in dilute alkalis; the addition of an acid to this solution causes a crystalline precipitate, consisting of long needles, which melt at 262°, and have the same composition as amidosulphoparabromobenzoic acid; their constitution appears to be that of *sulphoparabromobenzamic acid*, $C_6H_3Br(SO_2OH).CONH_2$.

The action of phosphorus pentachloride on sulphoparabromobenzoic acid gives rise to the dichloride, but this is readily decomposed by water; the chlorine, which is combined with the CO group being displaced by OH, producing the monochloride, $C_6H_3Br(SO_2Cl).COOH$. That this is really the case is conclusively shown by the action of zinc-dust on the alcoholic solution of the monochloride, which gives rise to two compounds: *sulphiparabromobenzoic acid*, $C_6H_3Br(SO_2H).COOH$, which is readily soluble in hot, but only very sparingly soluble in cold water, and *sulphibromobenzaldehyde*, $C_6H_3Br(SO_2H).COH$, which dissolves in warm water, but is partly thrown down again on boiling. The acid forms small colourless needles, which melt at 238°, with partial decomposition. It is a powerful bibasic acid, and forms crystalline salts. The aldehyde, which may be purified by repeated crystallisation of the barium salt, crystallises in long broad plates, melting at 131°. It is both an aldehyde and a monobasic acid: its barium salt forms large colourless prisms, which rapidly effloresce, and are only slightly soluble in cold water. The compound of the aldehyde with hydrogen sodium sulphite crystallises in long needles, melting at 78°. Besides this acid and aldehyde, other compounds are produced by the action of zinc on the monochloride, but they have not yet been investigated. E. N.

Trisulpho-oxybenzoic Acid. By M. KRETSCHY (*Deut. Chem. Ges. Ber.*, xi, 858—864).—Trisulpho-oxybenzoic acid is prepared by heating a solution of 10 grams of benzoic acid in 20 grams of sulphuric acid, with 15 grams of phosphorus pentoxide and 20 grams of sulphur trioxide in sealed tubes at 250° for five hours. The contents of the tubes are boiled with water to expel sulphur dioxide, and the sulphuric and phosphoric acids are removed by the addition of calcium carbonate. To obtain the free acid, basic acetate of lead is added to the filtrate, and the precipitated lead salt decomposed by sulphuretted hydrogen.

Trisulpho-oxybenzoic acid is a yellow syrupy hygroscopic liquid, which contains 4 mols. of water after drying at 100°. Both the acid and its salts produce an intense carmine coloration with a drop of ferric chloride, which disappears on the addition of sodium carbonate.

The basic lead salt $(C_7HS_3O_{12})_2Pb_5 + 6H_2O$, forms white opaque needle-shaped crystals, which lose their water of crystallisation at 235°. By the partial decomposition of this compound by sulphuretted hydrogen the neutral lead salt, $C_7H_2S_3O_{12}Pb_2 + 8H_2O$, is obtained. Basic potassium trisulpho-oxybenzoate, $C_7HS_3O_{12}K_5 + 2H_2O$, crystallises in monoclinic prisms; the neutral salt, $C_7HS_3O_{12}K_4 + 2H_2O$, separates out on the addition of alcohol to trisulpho-oxybenzoic acid, which has been nearly neutralised with potassium carbonate.

The barium salt, $C_7H_2S_3O_{12}Ba_2$, is decomposed by long-continued heating at 100°, or by boiling with barium carbonate; barium sulphate and barium disulpho-oxybenzoate, $(C_7H_3S_2O_9)_2Ba_3 + 8H_2O$, being formed in the latter case.

Trisulpho-oxybenzoic acid appears to be completely destroyed by fusion with potash, as only traces of pyrogallic and oxalic acids could be detected in the fused product. Attempts to replace the hydrogen in this acid by bromine were unsuccessful, the acid splitting up into monobromodisulpho- and dibromomonosulpho-benzoic acids.

W. C. W.

Iso-oxycinnamic Acid from Carvacrol. By O. JACOBSEN (*Deut. Chem. Ges. Ber.*, xi, 1058—1062).—Pure *cymenesulphonic acid*, $C_6H_3(CH_3)(C_3H_7).SO_3H + 2H_2O(1 : 4 : 2)$, from camphor cymene, forms large tabular colourless crystals, insoluble in dilute sulphuric acid. The *barium salt* $(C_{10}H_{13}.SO_3)_2Ba + 3H_2O$, crystallises in plates, which are sparingly soluble in cold water. The *sodium salt*, $C_{10}H_{13}SO_3Na + 5H_2O$, is deposited from an aqueous solution in large rhombic tables, which effloresce at the ordinary temperature, and lose all their water of crystallisation at 100°. By distilling sodium cymenesulphonate with sulphuric acid, pure cymene is obtained; b. p. 175—175·5° under 763 m.m. pressure, sp. gr. 0·8718 at 0°, and 0·86035 at 10°. Cymene has no action on polarised light. Its coefficient of refraction at 10° is 1·4915 for the D line.

Carvacrol prepared by gently fusing sodium cymenesulphonate with potash is a colourless liquid, which, when cooled to $-20°$, solidifies to a crystalline mass melting between $-3°$ and $0°$. Carvacrol boils at 237°; its sp. gr. is 0·98558 at 15°, and its coefficient of refraction for the D line is 1·5252 at 10°.

By continued fusion with potash, carvacrol is converted into *iso-oxycinnamic acid*, $C_{10}H_{12}O_3$, which is easily obtained in a state of purity by acidifying the crude product, and distilling in a current of steam. Iso-oxycinnamic acid separates out in flat needle-shaped crystals (m. p. 93°), when hydrochloric acid is added to a warm dilute solution of one of its salts. The acid is slightly soluble in cold water, but it dissolves freely in alcohol, ether, chloroform, and in hot water; the cold aqueous solution produces an intense reddish-violet coloration with ferric chloride. The *barium salt* crystallises in anhydrous rhombic tables, which are sparingly soluble in water. The *calcium salt* forms very soluble silky needles, which do not contain water of crystallisation. *Potassium iso-oxycinnamate* is very soluble in water, but crystallises well; it gives with zinc, manganese, cadmium and silver, salt precipitates, which dissolve in boiling water, and crystallise out on cooling. The copper and mercuric salts are likewise soluble in hot water.

Iso-oxycinnamic acid decomposes when heated alone to 235°, or by the action of hydrochloric acid at 190°, metapropylhydroxylbenzene being formed. This compound boils at 228°, and on cooling solidifies to a crystalline mass (m. p. 26°), almost insoluble in water. Ferric chloride produces in the aqueous solution, a faint blue; in the alcoholic solution, a green; and with the sodium or barium salts, a violet-red coloration.
W. C. W.

Synthesis of Phenylated Fatty Acids. By M. CONRAD (*Deut. Chem. Ges. Ber.*, xi, 1055—1058).—When sodium ethylate acts on ethylic benzylacetacetate, sodium-benzylacetacetic ether is formed, which is converted into methylbenzylacetacetic ether by heating with methyl iodide. *Methylbenzylacetacetic ether*—

$$CH_3.CO.C(CH_3.)(C_7H_7)(COOC_2H_5),$$

is a colourless liquid of aromatic odour (sp. gr. 1·046 at 23°, b. p. 287°).

Methylbenzylacetic acid is obtained by saponifying the preceding compound with concentrated potash solution; the alkaline liquid is acidified with sulphuric acid, and extracted with ether. On evaporating the ethereal solution, the acid remains as a crystalline mass, which is sparingly soluble in cold, but readily soluble in hot water. The acid melts at 34°, and boils at 275°. A solution of sodium methylbenzylacetate does not produce a precipitate with calcium or barium salts; with silver nitrate it gives a crystalline precipitate, sparingly soluble in boiling water; it also precipitates zinc and copper salts.

Benzylic methylbenzylacetate or *Methylhydrocinnameïn*, obtained by heating an alcoholic solution of benzyl chloride and potassium-methylbenzylacetate for ten hours, is a colourless liquid boiling at 53°. *Ethylbenzylacetacetic ether* is a colourless liquid boiling at 295—298°, which is prepared by the action of ethyl iodide on sodium-benzylacetacetic ether. Ethylic benzylacetosuccinate—

$$CH_3.CO.C(CH_2.COOC_2H_5)(C_7H_7)(COOC_2H_5),$$

produced by the action of sodium ethylate on benzyl chloride and ethyl acetosuccinate, boils at 310°, and has a specific gravity of 1·088 at 15°.

W. C. W.

A New Constituent of Coto Bark. By J. JOBST and O. HESSE (*Deut. Chem. Ges. Ber.*, xi, 1031—1034).—Coto bark, which has been previously extracted with ether, is digested with milk of lime, and the alkaline solution is acidified with hydrochloric acid, and agitated with ether. The residue obtained on evaporating the ethereal solution is dissolved in hot alcohol, which on cooling deposits a white crystalline powder, melting at 229°, and beginning to sublime at 210°. This substance was recognised as piperonylic acid, $C_8H_6O_4$, by the properties of several of its salts and by its reactions with sodium amalgam, potassium permanganate, baryta-water, bromine, and dilute hydrochloric and sulphuric acids. Piperonylic acid dissolves in cold concentrated sulphuric acid, forming a yellow solution, which rapidly turns brown, and finally black. No gas is evolved during the process. Water produces in the yellow solution a yellow, and in the black solution a black precipitate, the filtrate in each case contains protocatechuic acid. The reaction, $C_8H_6O_4 = C + C_7H_6O_4$, is incorrect, since protocatechuic acid is formed in the solution before any carbon separates out.

Mielch and Fittig (*Annalen*, clii, 40) obtained oxalic and carbonic acids by the oxidation of piperonylic acid with nitric acid; but if concentrated nitric acid is only allowed to act on the acid for a few minutes, a mixture of nitropiperonylic acid and methylenemononitropyrocatechin is formed. When piperonylic acid is added in small quantities to fuming nitric acid cooled down to 0°, carbon dioxide is given off, and methylenedinitropyrocatechin is produced. In each case the nitro-products are precipitated from the acid mixture by the addition of caustic soda. *Nitropiperonylic* or *methylenenitroprotocatechuic acid*, $C_8H_5(NO_2)O_4$, crystallises in yellow scales (m. p. 172°), which dissolve easily in water, and on the addition of caustic soda or potash to the aqueous solution a yellow coloration is produced, which turns blood-red on boiling. With ferric chloride no change is produced. This acid is monobasic; it forms well-crystallised salts, which burn vigorously when ignited.

Methylenemononitropyrocatechin, $C_7H_5(NO_2O)_2$, is deposited from a hot aqueous solution in pale yellow needles (m. p. 148°), which are insoluble in cold soda solution, but dissolve, on heating, with blood-red coloration. Ferric chloride does not produce any change.

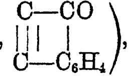
Methylenedinitropyrocatechin, $C_7H_4(NO_2)_2O_2$, which resembles the preceding compound in its behaviour with ferric chloride, and with soda, forms yellow plates or prisms, which melt at 100°, and burn when heated.

W. C. W.

Reduction of Ellagic Acid by Zinc-dust. By L. BARTH and GOLDSCHMIEDT (*Deut. Chem. Ges. Ber.*, xi, 846—850).—The ellagic acid was prepared from divi-divi (*Caesalpina coriaria*) by a modification of Lowe's process (*Zeit. Anal. Chem.*, xiv, 35). The alcoholic extract of the pods is concentrated, and the residue poured into water, when ellagic acid separates out. The filtrate is evaporated down to a syrup, and then treated with hot water and filtered. The residue yields tolerably pure ellagic acid on washing with hot alcohol.

When a mixture of ellagic acid with 15 times its weight of zinc-dust is submitted to a barely visible red heat in a current of hydrogen, traces of a diphenyl and of a red body are formed, but the chief product of the reaction is a hydrocarbon, $C_{13}H_{19}$ (m. p. 113°), which is shown by its compounds with bromine and with picric acid to be identical with fluorene. The nitro-product, $C_{13}H_8(NO_2)_2$, forms yellowish needle-shaped crystals, soluble in nitric acid, but insoluble in most of the usual solvents. When heated to 200° it turns brown, and at 255—260° it melts with decomposition. The properties of this body do not agree with those of Barbier's compound, but the discrepancy is attributed by the author to the presence of mononitro-products in Barbier's dinitro-derivative. W. C. W.

Action of Dehydrating Agents on Acid Anhydrides. By S. GABRIEL and A. MICHAEL (*Deut. Chem. Ges. Ber.*, xi, 1007—1021).

Derivatives of Phthalylacetic Acid.—The yellow compound, obtained as a bye-product in the preparation of phthalylacetic acid, and also formed by the action of strong sulphuric acid on phthalylacetic acid, may be regarded as ortho-tribenzoylbenzene, $C_6(C_6H_4.CO)''_3$ (a polymeride of benzoylacetylene,  $\left.\begin{array}{l}C\text{—}CO\\ \|\!|\quad |\\ C\text{—}C_6H_4\end{array}\right)$, since it yields phenenyltribenzoic acid, $C_6H_3(C_6H_4.COOH)_3$, on fusion with potash. This acid crystallises in colourless prisms (m.p. 259—261°) which dissolve easily in alcohol, ether, glacial acetic acid, and in alkalis, but are only sparingly soluble in benzene and carbon bisulphide. Engler and Heine's triphenylbenzene (*Ber.*, vi 638, and vii, 1123) is formed at a low red heat by the action of lime on phenenyltribenzoic acid.

Action of Bromine on Acetophenone-carbonic Acid.—In presence of water bromine converts phthalylacetic acid into tribromacetophenone-carbonic acid, $CBr_3.CO.C_6H_4.COOH$; but when a mixture of bromine, glacial acetic acid and acetophenone-carbonic acid is heated in sealed tubes at 100° bromomethylene is formed, $C_9H_8O_3 + Br_2 = C_9H_5BrO_2 + HBr + H_2O$. The contents of the tubes are heated on a water-bath to expel hydrobromic and acetic acids, and the residue is dissolved in hot alcohol. On evaporating the alcoholic solution, bromomethylenephthalyl crystallises out, and after diluting the mother-liquor with water an oily liquid separates, which on boiling with water deposits a yellow crystalline mass, having the composition $C_9H_6O_3$; this melts at 145—146°, and begins to sublime at 100°. *Bromomethylenephthalyl*—

$$C_6H_4(CO)_2CHBr,$$

dissolves easily in benzene, chloroform, carbon bisulphide, glacial acetic acid, and in hot alcohol; it crystallises in long flexible needles, which melt at 132—133°.

Attempts to replace the bromine by hydrogen, by the action of reducing agents, proved unsuccessful.

An addition product, $C_9H_5BrO_2.Br_2$, is obtained by digesting bromomethylenephthalyl with a solution of bromine in chloroform at 100°. This compound forms brilliant colourless crystals (m. p. 118°), which dissolve readily in benzene, carbon bisulphide, chloroform, glacial acetic acid, and in hot alcohol.

α-Phthalylpropionic acid, $C_6H_4(CO)_2\!=\!C_2H_3.COOH$.—The residue obtained by heating a mixture of sodium propionate with phthalic and propionic anhydrides is dissolved in boiling acetic acid (10 per cent.), and filtered while hot; on cooling, α-phthalylpropionic acid separates out in slender needles (m. p. 245—248°).

Phthalylpropionamide, $C_{11}H_7O_3.NH_2$, separates in iridescent scales (m. p. 193—195°), when an acid is added to a hot solution of phthalylpropionic acid in ammonia. *Propiophenonecarbonic acid*,

$$COOH.C_6H_4.CO.C_2H_5,$$

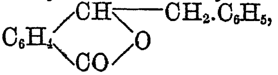
is formed when phthalylpropionic acid is boiled with excess of potash solution, $C_{11}H_8O_4 + H_2O = C_{10}H_{10}O_3 + CO_2$. This acid crystallises from its alcoholic solution in slender colourless needles, which melt at 91—92°. The silver salt, $C_{10}H_9AgO_3$, also forms long needle-shaped crystals. Phthalylpropionic acid is converted, by the action of phosphorus and strong hydriodic acid, into ortho-propylbenzoic acid, $COOH.C_6H_4.CH_2.CH_2.CH_3$; thus: $C_{11}H_8O_4 + H_4 = C_{10}H_{12}O_2 + CO_2$. This substance, which is easily soluble in the usual solvents, forms crystalline scales, melting at 58°.

Action of Sodium Acetate on a Mixture of Phthalic Anhydride and Phenylacetic Acid.—When a mixture of these three substances is heated, carbon dioxide is evolved, and a residue remains, which, after treatment with hot water and with dilute ammonia, dissolves in boiling alcohol. The alcoholic solution on cooling deposits colourless prisms (m. p. 98—99°) of *benzylidenephthalyl*, $C_{15}H_{10}O_2$. Its formation is represented by the following equation:—

$$C_6H_4(CO)_2O + C_6H_5.CH_2.COOH = C_6H_4(CO)_2CH.C_6H_5 + CO_2 + H_2O.$$

This body is insoluble in hot water and in dilute ammonia; it dissolves, however, in boiling alcohol, and in hot aqueous ammonia or potash solution. On the addition of an acid to the solution in caustic alkali, *orthodeoxybenzoïncarbonic acid*, $COOH.C_6H_4.CO.CH_2.C_6H_5$, separates out in the liquid state, but solidifies when left at rest for several hours.

The pure acid is soluble in alcohol, and is deposited from a boiling aqueous solution in long shining prisms (m. p. 74—75°) containing 1 mol. of water of crystallisation, which is expelled at 50°. The silver salt, $C_{15}H_{13}AgO_4$, is indistinctly crystalline. *Ortho-dibenzylcarbonic acid*, $COOH.C_6H_4.CH_2.CH_2.C_6H_5$, formed by the action of hydriodic acid on ortho-deoxybenzoïncarbonic acid at 190°, is deposited from its solution in alcohol in large tabular crystals, which are insoluble in water, but dissolve readily in alkalis. The aqueous solution of ammonium ortho-dibenzylcarbonate produces with lead and silver salts a white precipitate, and with copper salts a pale-blue precipitate.

Dibenzyl is formed by cautiously heating the silver salt. Ortho-deoxybenzoïncarbonic acid yields the anhydride of *ortho-toluylene-hydrate-carbonic acid*,  $C_6H_4\left<\begin{array}{l}CH\text{—}CH_2.C_6H_5,\\ \qquad\ >O\\ CO\end{array}\right.$ on treatment with sodium-amalgam.

The anhydride crystallises in long colourless needles (m. p. 56—57°), soluble in alcohol, ether, and in hot alkalis, but insoluble in water.

W. C. W.

Derivatives of η-Dichloro-Naphthalene. By P. T. CLEVE (*Bull. Soc. Chim.* [2], xxix, 499—501).—By the action of nitric acid under pressure, on η-dichloro-naphthalene at 150°, a solution is obtained, which on evaporation leaves a yellow crystalline mass, very soluble in water; this is a mixture of monochloro-phthalic and monochloro-nitro-phthalic acid. Monochloro-phthalic anhydride melts at 89°.

η-Dichloro-nitro-naphthalene, $C_{10}H_5Cl_2.NO_2$, is obtained by acting on a solution of the dichloride in acetic acid with fuming nitric acid. It crystallises in golden-yellow needles, sparingly soluble in alcohol and glacial acetic acid; it melts at 119°.

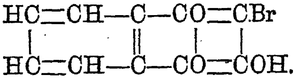
η-Dichloro-naphthylamine, $C_{10}H_5Cl_2.NH_2$, is formed by the reduction of the preceding nitro-compound with tin and hydrochloric acid. It crystallises in reddish needles, sparingly soluble in water, but readily in alcohol; it melts at about 94°.

ε-Trichloro-naphthalene, $C_{10}H_5Cl_3$.—This body, which is obtained by the action of PCl_5 on the mono-nitro derivative, crystallises in colourless needles, soluble in alcohol and melting at 65°; it contains at least one atom of chlorine in the β-position; two of the chlorine atoms are in the same benzene nucleus.

L. T. O'S.

Dibromonaphthaquinone and Bromoxynaphthaquinone. By T. DIEHL and V. MERZ (*Deut. Chem. Ges. Ber.*, xi, 1064—1069).—To prepare dibromonaphthaquinone, $C_{10}H_4Br_2O_2$, 7 parts of bromine are added by degrees to a boiling mixture of water, iodine (2 parts), and α-naphthol (1 part), or dinitronaphthol, contained in a flask connected with an upright condenser; the resinous product is dissolved in boiling alcohol or glacial acetic acid, and on cooling orange-coloured crystals (m. p. 149·5°) separate out. The bromoquinone, after it has been purified by sublimation or recrystallisation, is of a bright yellow colour. The sublimed substance melts at 151°, and is sparingly soluble in water, benzene, ether, and cold alcohol or glacial acetic acid. A warm soda-solution converts dibromonaphthaquinone into bromonaphthalic acid or *bromoxynaphthaquinone*, $C_{10}H_4Br.O_2.OH$, which separates out as a yellow flocculent precipitate on adding hydrochloric acid to the red alkaline solution. This compound is more easily obtained by the action of 3 parts of bromine on 2 parts of oxynaphthaquinone dissolved in glacial acetic acid; the addition of iodine facilitates the action. It is almost insoluble in water, benzene, and ether, but dissolves freely in a mixture of light petroleum and common ether; also in alcohol. It is deposited from a hot alcoholic solution in golden scales or needles (m. p. 196·5°).

The oxyquinone forms metallic derivatives by reaction with bases. $C_{10}H_4BrO_3K + 4H_2O$ crystallises in dark-red needles, easily soluble; $(C_{10}H_4BrO_3)_2Ba$ separates out as an orange-coloured crystalline precipitate, soluble in 1464 parts of water at 13°, when barium chloride is added to a solution of the preceding compound; $C_{10}H_4BrO_3Ag$ is a cherry-red insoluble powder. The potassium compound gives with a solution of alum an orange precipitate; with ferric chloride, red; with lead acetate, brick-red; with mercuric chloride, orange; and with cupric sulphate, red precipitates. Bromoxyquinone yields phthalic acid on evaporation with dilute nitric acid. Its constitution is analogous to that of chloroxynaphthaquinone, and may be represented thus:—



$$\begin{array}{l} HC{=}CH{-}C{-}CO{=}CBr \\ \;| \qquad\quad\;\; \| \quad\;\, | \quad\;\; | \\ HC{=}CH{-}C{-}CO{=}COH. \end{array}$$

Colourless crystalline scales, melting at 175° and having the composition $C_{10}H_6Br_2O_3$, are formed by the action of bromine on diamidonaphthol in presence of water. Attempts to prepare dioxynaphthaquinone from bromoxynaphthaquinone were unsuccessful.

W. C. W.

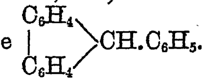
Nitro-derivatives of Alizarin. By S. GRAWITZ (*Bull. Soc. Chim.* [2], xxix, 501—502).—The author claims priority in pointing out the resemblance in the behaviour of phenol and alizarin when treated with nitric acid. L. T. O'S.

Madder Colouring Matters. (*Dingl. polyt. J.*, ccxxviii, 263—265).—Quantitatively, pseudo-purpurin is the most important colouring matter in madder next to alizarin, and has hitherto been regarded as a tetraoxyanthraquinone of the formula $C_{14}H_8O_6$. Rosenstiehl, however, found that this colouring matter evolves carbonic acid when heated at 180°, forming purpurin with a loss of 14·4 per cent. in weight. The new formula which he gives to pseudo-purpurin is $C_{15}H_8O_7$, according to the equation $C_{15}H_8O_7 = CO_2 + C_{14}H_8O_5$, it is therefore purpurincarbonic acid. This new formula agrees perfectly well with various reactions characteristic of this colouring matter, and also explains why Rosenstiehl did not succeed in obtaining pseudo-purpurin by oxidising purpurin. Plath and Liebermann have obtained the same results independently, and mention that when pseudo-purpurin or Kopp's commercial purpurin is boiled for a short time with potash solution, it is transformed into purpurin, which, after precipitation with acids and crystallisation from dilute alcohol, may be obtained in needles containing water of crystallisation, $C_{14}H_8O_5 + H_2O$, characteristic of pure purpurin. On treating pseudo-purpurin suspended in water with bromine, monobromopurpurin with 23·79 per cent. of bromine (calculated 23·88 per cent.) is obtained in the form of fine red needles melting at 275°, whilst carbonic dioxide escapes. A body, which is identical with Liebermann and Giesel's triacetylpurpurin, was obtained by heating pseudo-purpurin with acetic anhydride at 180°. Plath gives a method of preparing (Schunk and Römer's) purpuroxanthincarbonic acid from commercial purpurin. For this purpose crude purpurin is suspended in glacial acetic acid and heated to boiling, after the addition of a few drops of fuming nitric acid. On adding water to the cooled solution, xanthopurpurincarbonic acid is precipitated, which, when recrystallised from chloroform, has the formula of purpuroxanthincarbonic acid. This latter body, and that which Rosenstiehl obtained by boiling pseudo-purpurin with water, may be decomposed into carbonic dioxide and purpuroxanthin. Rosenstiehl also thinks that this compound may be obtained by reduction from pseudopurpurin, *i.e.*, purpurincarbonic acid, in the same manner as purpuroxanthin from purpurin—

$$\begin{array}{ccc} C_{15}H_8O_7 - O & = & C_{15}H_8O_6 \\ \text{Pseudopurpurin.} & & \text{Madder orange.} \\ C_{14}H_8O_5 - O & = & C_{14}H_8O_4 \\ \text{Purpurin.} & & \text{Purpuroxanthin.} \end{array}$$

D. B.

Constitution of the Hydrocarbon derived from Chlorotriphenylmethane. By W. HEMILIAN (*Deut. Chem. Ges. Ber.*, xi, 837—840).—Chlorotriphenylmethane, prepared by the action of phosphorus pentachloride on triphenylcarbinol, splits up into hydrochloric acid and a hydrocarbon, $C_{19}H_{14}$, on heating to 200°. The same change takes place at a lower temperature in presence of metallic zinc. The hydrocarbon purified by recrystallisation from glacial acetic acid and from alcohol forms fine silky needles (m. p. 145·5°), and is identical in all respects with diphenylenephenylmethane (*Ber.*, xi, 202). On oxidation with a mixture of sulphuric acid and potassium dichromate, it yields carbon dioxide and orthobenzoylbenzoic acid (Zincke and Plaskuda, *ibid.*, vi, 906, and vii, 986). The constitution of this hydrocarbon will consequently be



$$\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array} > CH.C_6H_5.$$

Orthobenzoylbenzoic acid dried at the ordinary temperature melts at 93—94°, but after drying at 110° its melting point rises to 127°.

W. C. W.

Products of the Decomposition of Gum Ammoniac Resin from Morocco by Fusion with Potash. By G. GOLDSCHMIEDT (*Deut. Chem. Ges. Ber.*, xi, 850—852).—The resin extracted from the crude material by treatment with alcohol, yields, when fused with potash, resorcin and a small quantity of a crystalline body, $C_{10}H_{10}O_6$, which melts at 265° with decomposition. This substance is sparingly soluble in water and in cold alcohol; it is more soluble in boiling alcohol and in ether. The aqueous solution is precipitated by lead acetate, and gives with ferric chloride a red coloration, which is turned to a claret colour by sodium carbonate, but is destroyed by hydrochloric acid.

The author regards this compound as identical with that which Hlasiwetz and Barth obtained (*Wien. Akad. Ber.*, li, 11) by fusing dragon's blood with potash, but as distinct from that obtained from berberine by similar treatment. Ordinary gum-ammoniac does not yield this acid on fusion with potash. W. C. W.

Bixin. By C. Etti (*Deut. Chem. Ges. Ber.*, xi, 864—870).—Bixin is prepared by digesting 1·5 kilos. of commercial annatto with 2·5 kilos. of 80 per cent. alcohol and 150 grams of sodium carbonate at 80°; the mixture is rapidly filtered and the residue is treated with 1·5 kilos. of 60 per cent. alcohol. On diluting the alcoholic extract with half its volume of water a portion of the sodium-bixin separates out, and the remainder is deposited after adding a saturated solution of sodium carbonate to the solution and leaving the mixture at rest for several days. The crystalline precipitate is purified by solution in hot 60 per cent. alcohol and reprecipitation by water and a solution of sodium carbonate. The purified sodium compound is finally decomposed by mixing it with alcohol and adding hydrochloric acid.

The mother-liquors from the sodium-bixin give a bulky red precipitate with hydrochloric acid, which is partly soluble in ether. The insoluble residue consists of amorphous bixin.

Bixin, $C_{28}H_{34}O_5$, is a dark-red lustrous body, consisting of long quadrangular microscopic plates; it melts at 175°, and is decomposed at higher temperatures. It is insoluble in water, sparingly soluble in ether, benzene, carbon bisulphide, and glacial acetic acid, but more soluble in chloroform and boiling alcohol.

Monosodium-bixin, $C_{28}H_{33}NaO_5 + 2H_2O$, forms dark-red iridescent crystals, which are soluble in dilute alcohol, but insoluble in absolute alcohol and in ether. On exposure to the air, they increase in weight and change to a pale red colour. The alcoholic solution is decomposed on continued boiling, and then deposits amorphous bixin on the addition of hydrochloric acid.

Disodium-bixin, $C_{28}H_{32}Na_2O_5 + 2H_2O$, separates out as a resinous mass, on boiling a mixture of bixin, dilute alcohol, and sodium carbonate for several hours.

Bixin forms crystalline compounds with potassium and with ammonium, but in solutions of barium and calcium salts it produces amorphous precipitates.

Strong sulphuric acid dissolves bixin, yielding a characteristic blue solution, which gives a dirty green precipitate on the addition of water.

Nitric acid and potassium permanganate attack bixin, forming oxalic acid. By the action of sodium-amalgam bixin is converted into a compound, $C_{28}H_{40}O_7$, and with hydriodic acid it yields $C_{28}H_{40}O_4$. On distillation with zinc-dust three hydrocarbons are formed, viz., metaxylene, C_8H_{10}; meta-ethyltoluene, C_9H_{12}; and a liquid, $C_{14}H_{14}$, boiling at 270—280°.

Amorphous bixin decomposes at 200° without melting; it contains more oxygen than the crystalline modification, which it resembles in its chemical properties. Its sodium and potassium compounds are not, however, precipitated by the addition of alkaline carbonates.

W. C. W.

Pelletierine, Alkaloïd of Pomegranate. By Tanret (*Compt. rend.*, lxxxvi, 1270—1271).—The bark of the pomegranate is roughly powdered and mixed with milk of lime to a thick paste, which is washed with water; the liquid is shaken with chloroform, which dissolves the pelletierine, and the chloroform solution is then treated with a dilute acid; the solution of a salt of the alkaloïd thus obtained is evaporated in a vacuum over sulphuric acid. To obtain the free base, the solution of one of its salts is treated with potassium carbonate and shaken with chloroform. The chloroform solution on evaporation leaves the alkaloïd as a colourless oily mass, boiling at about 180°, very soluble in water, alcohol, or ether, and especially in chloroform. It has an alkaline reaction, and precipitates most of the metals from their salts. It is precipitated by baryta, the precipitate being soluble in excess of the reagent. A precipitate is also produced by bromine-water in excess; by Nessler's reagent; by iodide of potassium and cadmium, and by phosphomolybdic acid. The sulphate, nitrate, and hydrochloride of pelletierine are crystalline and excessively hygroscopic. L. T. O'S.

Chemistry of Vegetable Physiology and Agriculture.

Estimation of Proteïds in Forage. By F. Sestini (*Gazzetta chimica italiana*, viii, 127—131).—The author urges that the method of calculating the value of different kinds of forage from a determination of the *total* amount of nitrogen they contain gives very fallacious results, their value as nitrogenous food-stuffs depending on the albuminoïd matters present. He recommends that the non-proteïds (nitrates, ammonic salts, amides, &c.) be removed by treatment with boiling water, which coagulates the vegetable albumin, adding a few drops of a concentrated solution of lactic acid or plumbic acetate to render the vegetable caseïn and similar albuminoïds insoluble. The nitrogen in the exhausted forage gives the amount of proteïds; the difference between this and that in the original forage gives the nitrogen present in other forms: this is often a very large proportion of the whole. C. E. G.

Liquorice Root. By F. Sestini (*Gazzetta chimica italiana*, viii, 131—137).—The author undertook an examination of liquorice root with a view to ascertain its effect on the soil in which it is grown. The following are the results of the analyses of the roots, both fresh and dried at 110°:—

	Fresh.	Dried at 110°.
Water	48·700	—
Fat, resin, and colouring matter (soluble in ether)	1·650	3·220
Glycyrrhizin	3·271	6·378
Starch, &c.	29·620	57·720
Cellulose	10·150	19·790
Proteïd matters	3·267	6·373
Ammonia (present as salts)	0·022	0·043
Asparagine*	1·240	2·416
Ash	2·080	4·060

* The nitrogen present otherwise than in ammonic salts or proteïds was calculated as asparagine.

The extract of liquorice usually contains 7—8·5 per cent. of ash and 15·5 to 17·5 of water. The fresh root completely exhausted with water, and the extract dried at 100°, gave:—

Water	48·7
Extract dried at 100°	25·4
Insoluble residue dried at 100°	25·9

but in practice it takes about five parts of the root to yield one of the extract, which moreover usually contains 15 per cent of water. The author suggests that the fibrous residue, which is at present burnt as fuel, might be utilized for paper-making. The following are analyses of the ash of the roots, the extract, and the insoluble residue.

	C.	CO_2.	SiO_2.	SO_3.	P_2O_5.	Cl.
Roots	0·37	22·44	10·02	2·86	0·82	1·23
Extract	1·52	12·30	14·85	0·49	4·64	4·24
Residue	0·87	15·89	47·46	0·30	0·13	trace

	CaO.	MgO.	Fe_2O_3.	K_2O.	Na_2O.
Roots	22·82	8·92	8·11	11·33	11·76
Extract	17·82	12·45	4·76	20·91	6·07
Residue	21·67	5·00	9·12	0·14	0·11

C. E. G.

Bats' Guano. By A. VOELCKER (*Jour. Roy. Agri. Soc.*, 1878, 60—72). This material is found in the caves inhabited by bats; large quantities have been discovered in Arkansas and Texas, and on the Bahama Islands; the deposits from the latter are known as Guanahani guano. Both texture and composition are very variable. Some specimens are light-coloured, dry, and powdery, and full of the undigested wings of insects. Other specimens are dark, damp, and lumpy, and of an earthy texture. The guano has very little odour. The following table shows the principal ingredients of a new and old deposit from caves in Arkansas, and the mean composition of eight cargoes imported from the Bahamas, with the highest and lowest percentages:—

	Arkansas Guano.		Bahama Guano.		
	Old deposit.	New deposit.	Highest per centages.	Lowest per-centages.	Mean.
Water	6·74	33·53	31·49	9·45	24·02
Organic matter	21·32	44·63	27·97	10·74	14·96
Ash	71·94	21·84	79·14	50·76	61·02
Nitrogen as organic matter and ammonia	2·48	6·62	1·93	0·53	0·89
Nitrogen as nitric acid	0·46	2·18	1·06	0·23	0·47
Total nitrogen	2·94	8·80	2·99	0·80	1·36
Phosphoric acid	6·64	3·76	21·09	4·59	13·49

As with most other guanos, the recent deposits are rich in nitrogen and poor in phosphates, while in the older and more decomposed deposits the proportion is reversed. Nitrates are present in all specimens. A small part of the phosphoric acid exists in the soluble form. The chief constituents of the ash, besides phosphates, are siliceous matter, and carbonate and sulphate of calcium, but the proportions are very variable. Analyses are given of bats' guano from Spain, Jamaica, and Penang, the latter is known as "Typelawer;" the composition of these specimens ranged nearly within the limits already given. R. W.

Purification of the Sewage-Water of Towns by Irrigation. (*Dingl. polyt. J.*, ccxxviii, 271—277).—In 1837 Paris possessed 67 kilometers, in 1850 130 kilometers, and at the present time 800 kilometers of sewers. The mouth of the main sewer at Clichy, and that of the smaller sewer at Saint Denis, pass about 3 cubic meters of dirty water into the Seine per second, or about 100,000,000 cubic meters in the year. These masses contain 125,000 tons of suspended substances, and are liable to putrid fermentation, as they contain 10 to 25 p. c. of organic substances, with 0·4 to 0·6 p. c. of nitrogen. 1 cubic meter of the water contains, besides these substances, nitrogen (Clichy) 40 grams, (Saint Denis) 140 grams; volatile or combustible substances 660 grams and 1,380 grams; inorganic substances 1400 grams and 1940 grams. Total (Clichy) 2,100 grams, (Saint Denis) 3,460 grams. According to a report in 1874, it is stated that the River Seine is contaminated very largely with animal and vegetable waste, and is covered with a fatty layer, becoming putrid, and evolving immense bubbles of gas, having a diameter of 1 to 1·5 m., and being composed of the following mixture:—Marsh-gas 72·88; carbonic acid 12·30; carbonic oxide 2·54; hydric sulphide 6·70; and various other gases 5·58 = 100·00 p. c. It is, therefore, not very remarkable to obtain 7·3 mgms. nitrogen in 1 litre of water, and only 1 c.c. of oxygen, whilst the pure river water contains 10·4 c.c. Purification trials with aluminium sulphate were made, but gave unsatisfactory results. By purifying sewage-water by irrigation, however, very satisfactory results were obtained, which formed the basis of some extensive works erected in the neighbourhood of Paris for purifying the water previous to its entering the river. At the present time a surface of 300 hectares of land is used for irrigation. The following figures show the improvement in the value of the soil on which irrigation has taken place. Soil irrigated is worth 400 to 500 francs per hectare, whilst ordinary soil fetches only 90 to 100 francs per hectare. The total quantity of nitrogen present in water after filtration by this method amounts only to 0·3 mgm. per litre. Purification of sewage-water by irrigation has been introduced in England, Germany, Belgium, Italy, Austria, and Spain.

In the second part of this paper a description is given of some experiments made by Schloesing and Muntz with regard to the fact that polluted water passing through a layer of quartz and chalk does not contain nitrates, the ammonia present remaining unaltered. The formation of nitrates which has been known to take place after a very long time, is, according to these experiments explained by the absorption of organised ferments, which can begin to act only after the development of their sporads, and is not due to atmospheric oxidation as generally supposed. The results of the experiments undertaken by Warington, Falk, and Jeannel, confirm the statements of Schloesing and Müntz. D. B.

Analytical Chemistry.

Use of Ammonium Thiocyanate in Volumetric Analysis. By J. Volhard (*Liebig's Annalen*, cxc, 1—61).—The author refers to a preliminary description of silver estimation by alkaline thiocyanates (*J. pr. Chem.* [2], ix, 217). More recent researches have proved that dilute standard solutions of the alkaline thiocyanates remain unaltered in strength for years in closed bottles, although a slight deposit often forms on standing; also that palladium and mercury are the only metals which interfere with the application of this method to silver estimation. Chlorine, bromine, and iodine, and other substances precipitable in acid solutions by silver salts, can also be readily determined by residual titration by this method; and methods which serve for the determination of copper exactly, and of mercury approximately, have also been worked out.

Part I. Silver Estimation.—In a solution of silver acidified with nitric acid, and containing a soluble ferric salt, an alkaline thiocyanate does not produce a permanent red colour until all the silver is precipitated as thiocyanate. Hence this method of precipitating silver can be used volumetrically with the ferric salt as indicator, provided the silver-value of the thiocyanate solution is previously determined by titration with a silver solution of known value.

A solution of ammonium thiocyanate is preferred on account of its freedom from chloride. According to the dampness of the salt, 7·5 or 8 grams are dissolved in a litre of water, and after finding the exact strength of this solution against a solution of silver nitrate, its standard is so corrected that 1 c.c. corresponds to 1 centigram of silver. The silver solution required for this purpose is made by dissolving half a gram of chemically pure silver in 8 or 10 c.c. of pure nitric acid (1·2 sp. gr.), then removing the nitrous acid by boiling and cooling: about 200 c.c. of water are added, and 5 c.c. of cold saturated iron-ammonium-alum solution, pure colourless nitric acid being added if necessary to remove the colour which the iron solution may impart to the liquid. The thiocyanate solution is then run in from a burette until the faintest light-brown colour appears in the liquid when viewed against a white wall. The point of complete precipitation is also indicated in this process, as in Gay-Lussac's, by the solution, after vigorous shaking, becoming quite clear.

The solution in which silver is to be estimated should be strongly acid with nitric acid, since the coloration given by thiocyanate with ferric salt is not interfered with by nitric acid, provided a sufficient quantity of the ferric salt is present. Pure nitric acid does not decompose the ferric thiocyanate, and unless nitrous acid or silver chloride is also present, the coloration is permanent. It is not necessary even to have approximately the same excess of acid in different titrations, but only to keep the proportion of the ferric salt to the volume of the liquid nearly constant. It must however be remembered that thiocyanic acid is oxidised, and that the ferric thiocyanate coloration is destroyed, by nitrous acid in the cold, or by nitric acid on warming. Hence nitric acid which has been partially decomposed by standing in the light, must before use be boiled for some time to remove the nitrous acid it contains; before being boiled, such acid, if mixed with ferric salt and a few drops of an alkaline thiocyanate, yields a coloration which gradually fades. The solution to be titrated must also be cold before the titration is commenced.

For the estimation of silver in alloys, the process may be carried out by dissolving a known weight of the alloy, and proceeding as above, or it may be modified according to Gay-Lussac's method. According to Gay-Lussac's volumetric method, a preliminary gravimetric determination would be made to determine approximately the percentage of silver; (this gravimetric may be replaced by a rough volumetric estimation made as described above). A quantity of the alloy is then employed for the exact volumetric estimation, which would contain somewhat over 1,000 milligrams of silver; the method is then modified by adding to this solution sufficient thiocyanate solution (instead of sodium chloride solution) to precipitate 1,000 milligrams of silver, and the final titration of the excess of silver is carried out with thiocyanate solution of one-tenth the usual strength, the final reaction being indicated by the ferric salt. The last half c.c. is not reckoned, as this represents the excess of thiocyanate required to produce the coloration. Should it be found that the solution for titration contains less than 1,000 milligrams of silver, and that the liquid is coloured before addition of the deci-thiocyanate solution, solution of silver nitrate of known strength is added until the coloration disappears, the quantity added is noted, and after the final titration with the deci-solution, the amount of silver thus added is subtracted. Gay-Lussac's tables can be employed in calculating the percentage of silver by this method.

The author finds that the only advantage in employing Gay-Lussac's principle is that the process can be carried out with greater precision, since smaller differences in the quantity of silver can be estimated by the use of the deci-thiocyanate solution than by the use of the stronger solution: also complete mixture of the solutions is more readily insured by a pipette than by a burette.

Part II. Estimation of Silver in presence of other Metals.—Copper.—This metal, usually present in silver alloys, may reach 70 per cent. without in the least affecting the accuracy of the method: if the percentage is higher, the final reaction becomes somewhat doubtful owing to the liquid becoming discoloured and opaque with copper thiocyanate. The interference of copper, however, renders Gay-Lussac's method useless when the copper reaches 50 per cent.; and Mohr's volumetric process with potassium chromate becomes impossible when any copper at all is present.

Should the proportion of copper in the alloy exceed 70 per cent., silver can be fused in known quantity with the alloy so as to reduce the proportion of copper, but the amount of copper used in the assay must never exceed 0·7 gram.

Another method, depending on the complete decomposition of silver thiocyanate by strong sulphuric acid, can also be employed. The silver is precipitated completely from the solution by an excess of thiocyanate solution, and after the subsidence of the precipitate the solution containing the copper is removed. This is most conveniently done by Carmichael's filter. The precipitate is covered with strong sulphuric acid and heated until it unites into black lumps: on addition of a few drops of strong nitric acid and warming, complete solution takes place. A little more nitric acid is added, all nitrous acid is removed by heating, and after dilution with 300 or 400 c.c. of water and addition of ferric salt, the silver is titrated as usual with the thiocyanate solution. The results are somewhat too high unless the sulphuric acid has first been removed by barium nitrate solution, since sulphuric acid lessens the delicacy of the final reaction.

Mercury.—If the thiocyanate solution be added to dilute mercurous nitrate solution containing ferric salt and some nitric acid, each drop produces a grey precipitate in a red cloud; both disappear on shaking. On adding much thiocyanate solution the grey precipitate becomes permanent; and on further addition of thiocyanate the red coloration remains. If silver nitrate be simultaneously present, the precipitate also disappears, since mercury prevents the permanent formation of the insoluble silver thiocyanate. Mercuric nitrate behaves like the mercurous salt, but in presence of much water yields no precipitate at all. Hence the presence of mercury in the silver solution renders the use of this method impossible. Fortunately mercury is easily removable from alloys.

Palladium.—Former researches (Rose and S. Kern) seem to prove that palladium yields no precipitate with alkaline thiocyanates: the author finds, however, that a pale-brown amorphous precipitate is obtained resembling ferric hydrate in colour, and that this is readily soluble in excess of the precipitant. Hence palladium would be reckoned with silver in the thiocyanate method and make the result too high: but palladium, although often present in silver, is contained in quantity too small to influence the result.

The other metals soluble in nitric acid to more or less colourless solutions, such as *lead*, *cadmium*, *thallium*, *bismuth*, *zinc*, *iron*, and *manganese*, do not in any respect influence the titration. The colorations due to cobalt and nickel salts render experience necessary to recognise the final reaction. At first one usually adds too much thiocyanate; the best plan is then to gradually titrate back with silver nitrate solution, when the sharp green or pink tint appears so distinctly that on again adding the thiocyanate solution the commencement of formation of ferric thiocyanate is sharply recognised by the change to yellowish-brown: after titrating backwards and forwards several times the change produced by the addition of half a drop of thiocyanate is recognisable at the end of the reaction. The colours of nickel and cobalt solutions are not truly complementary, but when mixed produce a brownish tint, which is more perplexing than green or pink: hence attempts to neutralise the colour of the one by addition of the other were given up. *Tin*, *antimony*, and *arsenic* in solution do not influence the results at all; even when the liquid is quite opaque with oxide of tin or antimony, the final reaction was perfectly evident.

Silver-assay results.—A table in the original paper gives a comparison of the results obtained from twenty-seven silver alloys by the usual Gay-Lussac method, and by the thiocyanate method carried out on one gram of the alloy. The results were obtained by H. Riederer, assayer to the Royal Mint. The numbers obtained by the two methods are identical in nearly half of these analyses, and the differences in the remainder are minute: hence the author concludes that the two methods are equally reliable. It is noteworthy, however, in favour of the new method, that a dry assay is not requisite, especially if a duplicate analysis is made: also that the laborious shaking required by Gay-Lussac's method is unnecessary, and the end of the reaction is more easily observed, especially by inexperienced workers. A much higher percentage of copper is allowable in the thiocyanate method, and turbidity from tin or antimony oxide, which would render Gay-Lussac's method entirely inapplicable, in no way interferes with the new method. With the precautions already given, the thiocyanate solution, although organic, runs no greater risk of alteration by decomposition than the inorganic sodium chloride solution used by Gay-Lussac. The new method is already employed in metallurgical laboratories, and will doubtless find its way into laboratories for mint assay.

Estimation of the Halogens.—The thiocyanate method is well adapted for estimating the halogens: by addition of excess of a standard silver solution the halogens are completely precipitated, and the excess of silver is estimated by the thiocyanate solution with ferric salt as indicator. A deci-normal solution of silver nitrate is used, and the thiocyanate solution is made to correspond to this by titration against it in presence of ferric salt.

Chlorine.—The only reason why the process requires any special description is, that silver chloride decomposes the thiocyanate solution. The author finds that silver chloride in every condition acts thus upon the thiocyanate: and that the whole of its chlorine passes into solution if thiocyanate solution in excess is added to ammoniacal solution of silver chloride, and the mixture is afterwards acidified with nitric acid. On the other hand, if the thiocyanate solution is dropped into a nitric acid solution containing silver nitrate and suspended silver chloride, together with the ferric salt as indicator, and the liquid is not shaken more than is necessary to secure complete mixture, the action on the silver chloride proceeds so slowly that the correctness of the result is not influenced. If, however, the agitation is violent and prolonged, the silver chloride, by decomposing a portion of the thiocyanate, will give results too low. It must further be remembered that after the pale-brown colour has once appeared, it is scarcely perceptibly increased in intensity by further addition of the thiocyanate: hence it is necessary to acquire by practice the power of at once recognising the first appearance of the tint. The weighed metallic chloride is dissolved in 300 or 400 c.c. of water, mixed with 5 c.c. of cold iron-alum solution, and with sufficient nitric acid to remove the colour imparted by the ferric salt; deci-normal solution of silver nitrate is then added in slight excess: the addition of the thiocyanate solution is then at once proceeded with, the liquid being constantly shaken and stirred round to secure rapid mixture; the titration is finished when the liquid retains its pale-brown colour after standing still for ten minutes. The number of c.c. of silver nitrate solution used, from which the number of c.c. of thiocyanate solution has been subtracted, if multiplied by 0·00355, gives the weight of chlorine present in grams. If the weight of chlorine in solution is not even approximately known, it is only necessary to add occasionally, while running in the silver nitrate solution, several drops of the standard thiocyanate solution; as long as the silver solution is not in excess, the colour produced by the thiocyanate disappears slowly; but as soon as excess has been added the colour caused by adding a drop of thiocyanate immediately vanishes, leaving the liquid milk-white. In calculating the result, the quantity of the standard thiocyanate thus used must be added to the quantity required for titrating the excess of silver, and the whole subtracted from the quantity of silver nitrate solution employed. The author does not recommend filtration from the silver chloride, since it occasions waste of time; neither is the employment of an aliquot part of the clear liquid after subsidence advisable, since the results thus lose in accuracy. After a little practice results may be obtained of sufficient precision to be valuable for atomic weight determinations. The process is undoubtedly more accurate than that of Mohr, and has the very decided advantage of being applicable to acid solutions.

Bromine.—Silver bromide acts upon thiocyanate solution to a far less extent than silver chloride does; in fact, experiments showed that the process applied to the estimation of bromine gave the final reaction at once and without difficulty; the results being very accurate. The point when excess of silver solution has been added can be judged with sufficient accuracy by the liquid becoming clear after being well shaken.

Iodine.—Silver iodide exerts no decomposing action on the thiocyanate; the process is, however, liable to be rendered inaccurate by silver iodide carrying down with it potassium iodide or silver nitrate, or both of these, and thus more or less withdrawing them from the reaction. To avoid this source of error, the following method of proceeding is necessary:—The iodide is dissolved in 300 or 400 times its weight of water in a stoppered bottle, and the silver solution is added to it until the precipitate coagulates on shaking; this shows that an excess of silver nitrate is present; 0·1 or 0·2 c.c. more of silver solution should then be added, and the liquid well shaken: by this means any unaltered iodide is converted into silver iodide. Either of two methods may then be used for completing the estimation: after addition of the ferric solution and nitric acid, thiocyanate solution is added until a decided coloration is obtained, and the liquid shaken until this colour disappears; the proceeding being repeated until a faint colour remains after shaking: or excess of thiocyanate is at once added, the liquid well shaken, and the thiocyanate in excess titrated by silver solution, which should be added either until a faint brown colour remains, or else in slight excess, the excess being then titrated back by thiocyanate. The latter method is the more rapid, but the two give almost identical results.

Estimation of the Halogens in Organic Compounds.—The thiocyanate method is remarkably suited to the estimation of halogens in organic substances, one of the ordinary methods of decomposition being employed, provided no loss of the halogen is incurred. Carius's method, modified by employing a known quantity of silver nitrate, may be used: the author considers it unsuitable for several reasons. During the violent escape of gas on opening the tube, some of the silver nitrate solution is very liable to be lost; further, it is extremely difficult to remove by washing all silver nitrate from the insoluble silver salt; there is also no means of ascertaining when the decomposition is complete. Combustion with lime, free from halogens, is quite trustworthy; but the author prefers mixing the substance with forty times its weight of a mixture of sodium carbonate with twice its weight of potassium nitrate, and burning in a covered crucible or in an inclined combustion-tube, according to the nature of the substance. These salts are chosen as being easily obtained free from halogens. In the case of very volatile substances, a layer of potassium nitrate is placed above the mixture which contains the substance, and is fused before heating the mixture.

Estimation of the Halogens when Thiocyanates are present.—To detect and separate the halogens, thiocyanates must first be destroyed. To effect this, when a chloride is present, the precipitate obtained by excess of silver nitrate in the solution acid with nitric acid is filtered off and well drained; then heated, together with the filter, with sulphuric acid diluted with half its volume of water, until the precipitate unites into black masses; a few drops of nitric acid are then added, and the heating continued. On diluting with water, all the chlorine remains as undissolved silver chloride, whilst the silver thiocyanate has been completely decomposed. Another plan is to dissolve 2 or 3 grams of the thiocyanate in 400 or 500 c.c. of water and heat on the water-bath, with occasional addition of nitric acid in small quantity as long as it produces any further reaction; the mixture is then further heated, supplying the water lost by evaporation, until a drop no longer gives the thiocyanate reaction with ferric salt solution decolorised by nitric acid. The liquid made alkaline with ammonia, is evaporated to two-thirds its bulk on the water-bath, and is then ready for precipitation by silver solution. Experiments prove that by proceeding thus, the thiocyanate is entirely destroyed, without loss of chlorine. If only a trace of chloride has to be detected, it is better to warm with nitric acid in a less dilute condition until evolution of gas ceases, add excess of sodium carbonate, evaporate to dryness, ignite the residue, take up with warm water and test with silver nitrate, after adding excess of nitric acid. The methods above described are inapplicable when bromine or iodine is present, as they would cause loss of these halogens. In that case, the silver precipitate may be digested in a sealed tube with nitric acid for three or four hours at 160°, and the liquid then diluted with water; or the substance may be fused with potassium nitrate and sodium carbonate, a large excess of the latter being used to avoid explosion. The latter method is better modified by mixing the substance with sodium carbonate, both being perfectly dry, and gradually dropping the mixture into fused potassium nitrate.

Separation of Chloride and Bromide.—If a mixture of silver chloride and silver iodide is mixed with ammonia in excess and sufficient ammonium thiocyanate, and is digested at ordinary temperatures for an hour, the chloride is completely decomposed, the iodide remaining quite unaltered. On acidifying with nitric acid and washing the precipitate, the chloride will be contained entirely in the filtrate along with thiocyanate; the iodide will remain as insoluble silver iodide, mixed with silver thiocyanate. By destroying the thiocyanate in the filtrate and precipitate respectively by the methods given above, the chloride may be titrated by the thiocyanate process, and the iodide weighed.

Cyanide.—Silver cyanide is too rapidly converted into silver thiocyanate in presence of thiocyanic acid, to render the thiocyanate method applicable without modification. The estimation is, however, quite exact if standard silver nitrate is added at once in excess, and the excess of silver nitrate is then titrated in an aliquot portion of the liquid filtered from the precipitate. With prussic acid of the pharmacopœia strength, the difficulty consists in avoiding loss by volatilisation of the acid during the process; the author recommends running in standard silver solution, in order to find how much is required before further addition ceases to precipitate. For this preliminary test, 5 c.c. of the prussic acid, diluted with 300 or 400 c.c. of water, are used. For the accurate titration, 5 c.c. of the prussic acid are then run at once into a somewhat larger quantity of the silver nitrate solution, and in a known fraction of the filtered mixture the silver is titrated by thiocyanate. This method is preferable to Liebig's only when the requisite standard solutions are in readiness. For Liebig's method the author prefers a centinormal silver solution which is weighed, to the decinormal run in from burettes. The weaker solution yields a finely-divided precipitate, which is much more rapidly dissolved by shaking than the curdy precipitate yielded by a stronger solution, and the quantity of silver nitrate employed is of course more accurately obtained from the more dilute solution.

Estimation of Copper.—The method consists in the complete precipitation of the copper as cuprous thiocyanate by excess of standard thiocyanate, and subsequent titration of this excess. Ferrous salt could not be used as a reducing agent. The author proceeds as follows:—The solution of copper, from which any large excess of nitric acid must be removed by evaporation, is mixed with sodium carbonate solution free from chlorine, until a slight permanent precipitate appears. Saturated aqueous sulphurous acid is then added; this causes the liquid to become clear; the solution is then heated to boiling, more sulphurous acid being added if the smell is not strongly perceptible. Standard thiocyanate is then run in until a greenish colour is no longer seen at the place where the thiocyanate enters the liquid; a further quantity of thioycanate is added to ensure excess. If the liquid is coloured by other metals, it is often necessary to allow the precipitate to settle, and test a small portion of the decanted liquid with more thiocyanate, to ascertain if the precipitation is complete, this portion being afterwards returned. The whole quantity of thiocyanate added is noted. The liquid, when cold, is made up to a measured volume, filtered, an aliquot part mixed with ferric salt and nitric acid, and the thiocyanate titrated with the silver nitrate standard solution. In solutions coloured with other metals, the end is often most easily noted by first carefully removing the ferric thiocyanate coloration by addition of silver nitrate, and then adding thiocyanate until the colour reappears. The method has not yet been tried for assays of ores, but it will doubtless be applicable, possibly with some modifications; the only substances which seem to interfere being the halogens, silver, and mercury. The advantages of the method are its accuracy, and the non-interference of other metals present in solution with the copper.

Mercury Estimation.—As already stated, the behaviour of solutions of mercuric salts towards thiocyanate is similar to that of silver salts; but on adding mercuric nitrate solution to a liquid coloured by ferric thiocyanate, more than an equivalent quantity is required to destroy the coloration, since mercuric thiocyanate is partially decomposed by solution of a ferric salt. Hence, on titrating with thiocyanate, a mercuric nitrate solution mixed with ferric salt and nitric acid, a brownish colour appears before a quantity of the thiocyanate equivalent to the mercury present has been added. The first appearance of the colour is noticeable, but it does not increase very perceptibly by further addition of thiocyanate. This deficiency in the result obtained is slight, but appears to vary with the conditions of dilution and acidity of the solution, and with the rate at which the thiocyanate is added. The results obtained are closely approximate and constant if the mercuric nitrate solution is first very nearly neutralised with pure sodium carbonate, and the thiocyanate solution is then added, until a brownish tint is obtained. The method is perhaps most useful in determining mercury in organic compounds which have been decomposed by Carius' method. Mercury can be thus estimated only when united with an acid radicle containing oxygen; mercuric chloride yields a coloration long before the equivalent quantity of thiocyanate solution has been added.

The author strongly recommends ammonium thiocyanate solution, titrated by silver solution, as a means of determining the oxidation value of permanganate solution. A molecule of this cyanic acid requires precisely three atoms of oxygen, passing into sulphuric anhydride and hydrocyanic acid: hence, 1 c.c. of the decinormal thiocyanate requires 4·8 milligrams. The measured thiocyanate solution is largely diluted and mixed with sulphuric acid, and the permanganate is then run in until its colour remains. The results agreed to one-tenth of a c.c. The ammonium thiocyanate is recommended for this purpose above all the solutions usually employed, on account of the unalterability of its dilute solution. F. C.

Estimation of Manganese, Lead, Copper, Zinc, and Nickel, and their Alloys. By A. Riche (*Ann. Chim. Phys.* [5], xiii, 508—543).—This method, which affords a rapid means of estimation, consists in decomposing salts of the above metals with the electric current, either in an acid or alkaline solution, and weighing the precipitated metal or oxide.

The apparatus consists of a platinum crucible, in which is suspended a hollow truncated cone of platinum foil with small openings in the side: in the case of manganese, however, this cone is replaced by a spiral of platinum wire. The cone or spiral serves as the negative pole, whilst the crucible acts as the positive. The decomposition may take place at the ordinary, or at a higher or lower temperature.

Estimation of Manganese.—If a solution of the nitrate, chloride, or sulphate of manganese, is subjected to the action of two or three Bunsen's elements, the manganese is deposited as dioxide on the positive pole; when the decomposition is complete (which is determined by taking out a drop and treating it with ammonium sulphide) the liquid is filtered, and any dioxide that may fall on the filter paper is washed back into the crucible. The oxide, together with the crucible spiral and filter paper, is ignited, and the manganese weighed as Mn_3O_4. In the case of the sulphate, no oxide is deposited on the negative pole, and consequently there is no necessity to weigh the spiral: it is therefore better to work with sulphate of manganese in presence of other metals which are deposited on the negative pole. In this way ·0005 gram Mn_3O_4 can easily be estimated, and ·0000025 gram Mn_3O_4 detected by the rose coloration which it shows. The presence of the salts of the alkali-metals and alkaline earths in no way interferes with the reaction.

In presence of excess of iron a deposit occurs on both poles, but when the current stops, the iron deposited on the negative pole dissolves as sulphate, which reduces the manganese dioxide, and redissolves it; it is therefore best, after oxidation, to precipitate the iron with barium carbonate, remove the excess of barium with sulphuric acid, evaporate the solution to dryness, dilute with water, and decompose as before. By this means manganese in blood, milk, or urine, may be detected and estimated.

Estimation of Lead.—In the case of lead, when an electric current is passed through a warm solution of the nitrate, the metallic lead which is sometimes deposited on the negative pole dissolves, and is redeposited on the positive pole as dioxide; but this deposit redissolves as soon as the current is stopped. To avoid this source of error, the liquid is syphoned off without any interruption in the current, the contents of the crucible dried at 105—120°, and weighed. Lead is readily estimated in presence of other metals, and may easily be separated from silver, which is deposited on the negative pole. In presence of formic and acetic acids the lead is deposited partly on the positive pole as dioxide, and partly on the negative pole as metal; oxalic acid, however, reduces it completely to metal, which is deposited on the negative pole.

Estimation of Copper.—The solution, which may contain sulphuric, nitric, or hydrochloric acid, is evaporated nearly to dryness, diluted with water, and a current passed through the solution at a temperature between 60 and 90°. The copper separates out on the negative pole as a red film, which is washed, and dried at 50 and 60°. To ascertain when all the copper is precipitated, a drop of the solution is treated with potassium ferrocyanide.

Copper and Manganese.—The liquid is first subjected to the action of one element, which completely precipitates the copper on the negative pole, and partially the manganese. The manganese dioxide is washed from the copper, and the liquid containing the manganese solution is then subjected to the action of two elements, which precipitate it as dioxide.

Copper and Iron.—It is necessary in this case to keep the temperature below 70° when nitric acid is present, otherwise the iron attaches itself to the copper, which is washed free with difficulty. This is also prevented by using sulphuric acid, or by saturating the solution with ammonia gas.

Copper and Silver.—If the silver is in excess, hydrochloric acid is added, and the clear solution is then saturated with ammonia, and submitted to the action of a Bunsen's element. If the amount of silver does not exceed ·01 gram it may be at once precipitated by a Leclanché's element on the negative pole, the copper being left in solution. The metallic silver is weighed; dissolved in acid, and the cone replaced, when the solution is subjected to the action of a Bunsen's element; the copper is then precipitated. Copper may be estimated in the warm solution in presence of acetic acid, and therefore may be determined in commercial vinegar by this method, as follows:—The vinegar is submitted directly to the action of the current, and if copper is present, a black deposit appears on the negative pole; this is dissolved in nitric acid, the solution evaporated to dryness, and the residue dissolved in water; from this solution pure copper is precipitated when a current is passed through it. Copper may also be estimated in presence of phosphoric and tartaric acids by dissolving the salts in a few drops of nitric acid, and passing a current from one element through the solution.

Estimation of Zinc.—Zinc is best estimated by evaporating the solution containing nitric acid with excess of sulphuric acid, saturating the residue with ammonia, adding five grams of ammonium sulphate, and finally acidifying with a few drops of sulphuric acid. Zinc is deposited from this solution as a very adherent bluish-white film on the negative pole when submitted to electrolyses with two Bunsen's elements. The author rejects the method formerly given by himself (*Académie des Sciences*, vol. viii, 226) on account of the slowness and difficulty in working it.

Zinc and Silver.—When the solution contains less than 0·01 gram of silver it may be separated from the zinc by subjecting the solution to a current from one Leclanché's element, when the silver is deposited on the negative pole.

Zinc and Copper.—By passing the current from one Bunsen's element through an ammoniacal or acid (sulphuric or nitric acid) solution, the copper is deposited on the negative pole. The solution containing the zinc is made acid with sulphuric acid, and a current from two elements passed, when the zinc is deposited on the negative pole.

Zinc and Iron.—In this case the iron must be precipitated with ammonia, and estimated as above.

Zinc and Manganese.—The solution is prepared as for the estimation of zinc, and a current from two Bunsen's elements passed through it, when the zinc is deposited on the negative pole; this is weighed and the manganese which is deposited on the positive pole is estimated as described above (*estimation of manganese*).

Zinc and Magnesium.—The estimation of zinc is effected by adding a few drops of acid to the solution and passing the current. If the deposit contains magnesium, it is dissolved in sulphuric acid, and the zinc precipitated in presence of ammonium sulphate.

Brass.—The alloy is dissolved in nitric acid, and the solution subjected to a current from one Bunsen's element, when the copper is deposited on the negative pole and the lead on the positive pole. The copper is weighed, and dissolved off the cone, which is replaced; the poles are then changed, and the lead deposited on the crucible is thus transferred to the cone and weighed as dioxide. The iron is precipitated as oxide and weighed, the solution is evaporated with sulphuric acid, and the zinc estimated as previously described (*estimation of zinc*).

Bronze.—Four or five grams are dissolved in nitric acid, and the tin estimated as oxide; the copper, lead, iron, and zinc, are estimated in the filtered solution as in the case of brass.

Estimation of Nickel.—Nickel is deposited from a slightly acid (sulphuric acid) solution at 60 or 80° by means of a current from two Bunsen's elements. Although the nickel is generally completely precipitated the first time, it is always as well to subject it to the action of the current a second time.

Nickel and Copper.—Only the copper is deposited when an acid (sulphuric or nitric acid) solution is subjected to the action of one Bunsen's element; the solution containing the nickel is made alkaline with ammonia, and then slightly acid; on passing the current the nickel is deposited.

Nickel and Lead.—The lead is first precipitated as dioxide from a nitric acid solution by means of a Leclanché's element, and the nickel is determined afterwards.

Nickel and Manganese.—The nickel is completely precipitated on the negative pole when a current is passed through an acid (sulphuric acid) solution; it is washed and weighed. The action is then continued, if necessary, until the manganese is completely precipitated as dioxide on the positive pole.

Nickel and Magnesium.—The separation is effected in a solution made acid with sulphuric acid.

The analytical results show the exactness and accuracy which attend this method. L. T. O'S.

Dissolving Ignited Ferric Oxide. By A. CLASSEN (*Zeitschr. Anal. Chem.*, xvii, 182).—The ignited ferric oxide is brought into the soluble state, by digesting or boiling the powdered oxide with dilute potash solution. E. W. P.

Estimation of Antimony. By F. BECKER (*Zeitschr. Anal. Chem.*, xvii, 185).—One part of the antimony-compound is fused in a porcelain crucible with a mixture of three parts sulphur and three parts sodium-potassium carbonate; the mass is then treated with water, and the dissolved antimony sulphide precipitated by hydrochloric acid, and determined in the usual way. E. W. P.

Guaiacum as a Test for Copper. By E. PURGOTTI (*Gazzetta chimica italiana*, viii, 104—107).—Schönbein had noticed that copper salts in presence of cyanides gave a blue colour with guaiacum, and the author has since found that ferrocyanides, nitroprussides, sulphocyanates, and cyanates, and also alkaline chlorides and chlorides of the alkaline earths produce the same effect as cyanides. On this reaction he has found a test for copper. The solution, which must be free from all substances, such as ferric salts, &c., which colour guaiacum blue, is mixed with a solution of an alkaline chloride and poured gently down the side of a test-tube containing an alcoholic solution of guaiacum; if the most minute trace of copper is present a blue colour is produced at the junction of the two liquids, and if the quantity of copper be larger the whole of the liquid becomes blue on agitation; in this way ·001 milligram of $CuSO_4.5H_2O$ in a decigram of water gives a distinct coloration. The action appears to be due to oxidation by the cupric chloride—

$$2CuCl_2 + H_2O = Cu_2Cl_2 + 2HCl + O.$$

C. E. G.

Water-analysis. Determination of Cellulose and Modified Cellulose in Drinking-water. By J. A. WANKLYN and W. J. COOPER (*Phil. Mag.* [5], 464).—This is a modification of Forchammer's permanganate process. The following is an outline of the method employed:—

A litre of the water is placed in a retort provided with a condenser, with 5 c.c. of a standard permanganate solution (0·4 mm. O per c.c.) and 5 c.c. of a standard caustic potash solution (5 per cent.) are added; the water is then rapidly distilled off and, if necessary, more permanganate added. When the volume is reduced to 100—200 c.c. and excess of permanganate remains, the distillation is stopped, the liquid acidified with sulphuric acid, excess of standard ferrous sulphate added, and the liquid titrated back with the standard permanganate. If necessary, more than 1 litre of water can be used. On applying the process the authors obtained the following results:—

	Oxygen consumed per litre of water.
Excellent distilled water	0·13 milligram.
Thames water from a water company..	2·30 „

This shows a striking difference between common drinking-water and pure water. Experiments with dilute solutions gave results approximating very nearly to theory; they will be given in a future communication.

C. W. W.

Note on Urea and Crenate of Ammonia in Spring Water. By T. L. PHIPSON (*Chem. News*, xxxvii, 233).—In testing water for urea, ammonium crenate, if present in any quantity, is apt to interfere. The ammonium crenate dissolved in water may be isolated by evaporating about a quart of the water to dryness on the water-bath and treating the residue with absolute alcohol. A small quantity of the alcoholic solution, after evaporation to a syrupy consistency, is treated with nitric acid; by this means crystals of urea nitrate will be formed if urea be originally present; failing the formation of urea nitrate, if ammonium crenate and free crenic acid (due to decomposition of the ammonia salt by heat) be present, the alcohol solution will be yellow, and on evaporation will leave an amorphous yellow mass, yielding a solution in water from which copper crenate may be precipitated.

E. W. P.

Testing for Morphine. By E. BURI (*Zeitschr. Anal. Chem.*, xvii, 185).—Instead of evaporating the amyl alcohol solution of morphine on the water-bath according to the Stas-Otto method, evaporation is allowed to take place spontaneously at the ordinary temperature, whereby well-developed crystals are obtained. If, however, the amount of the alcohol is considerable, it is advisable to evaporate to dryness at 100°, treat the residue with acidulated water, saturate the clear solution with ammonia, and finally dissolve out the alkaloïd with amyl alcohol; this solution may then be allowed to evaporate spontaneously.

E. W. P.

Adulteration and Testing of Beer. By A. SCHMIDT (*Arch. Pharm.* [3], xii, 392—422).—A very lengthy paper, containing details of the methods for testing beer well known to analysts.

M. M. P. M.

Determination of Water and Fat in Milk. By W. C. HERAEUS (*Arch. Pharm.* [3], xii, 443).—Ten grams of the sample is mixed with powdered glass in a small silver boat, which is placed within an iron tube, one end of which is connected with a Bunsen's pump and the other with a glass tube containing caustic lime; air at a temperature of about 35° is drawn over the milk for 30 minutes, at the expiration of which time the milk is completely dry. The residue is treated with petroleum ether and the fat determined from the loss.

M. M. P. M.

Technical Chemistry.

Decomposition of Sulphur-lyes from Soda-waste by Hydrochloric Acid. By G. LUNGE (*Dingl. polyt. J.*, ccxxviii, 252—263).—It is known that the yellow lyes, "sulphur lyes," obtained by the oxidation of soda residues in the air are worked up in two different ways, viz., in Schaffner's double-boiler apparatus, or in Mond's decomposition-vat.

According to the first process sulphurous acid is passed into the lyes, which converts all the sulphide into thiosulphate, the latter being then decomposed by hydrochloric acid, which precipitates sulphur, and leaves calcium chloride in solution, whilst sulphurous acid escapes. The latter is used for saturating further portions of the lye. The following equation gives the reaction taking place:—

$$CaS_2O_3 + 2HCl = CaCl_2 + S + SO_2 + H_2O.$$

Mond, however, prefers to treat the liquors containing 1 molecule of thiosulphate to 2 molecules of sulphide directly with hydrochloric acid in order to obtain the following reaction:—

$$2CaS + CaS_2O_3 + 6HCl = 3CaCl_2 + 4S + 3H_2O.$$

He objects to Schaffner's method of treatment, and adds that only a very small quantity of sulphurous acid is obtained in the second part of his operation, and that instead of this acid large quantities of sulphates are formed. Calcium thiosulphate and hydrochloric acid form in the first place sulphur and trithionate, the latter being then decomposed into sulphur, sulphate, and sulphurous acid, thus:—

$$5CaS_2O_3 + 6HCl = 3CaCl_2 + 2CaS_3O_6 + 4S + 3H_2O$$
$$3CaS_3O_6 + 4HCl = CaSO_4 + 2CaCl_2 + 6SO_2 + 2S + 2H_2O.$$

The sulphurous acid liberated in the last reaction converts further portions of undecomposed thiosulphate into trithionate, according to the known equation, $2CaS_2O_3 + 3SO_2 = 2CaS_3O_6 + S$. The newly-formed trithionate is again decomposed according to the former equations, the same series of reactions being repeated. Besides the sulphur, much calcium sulphate is obtained, and but very little sulphurous acid.

Schaffner's views are much opposed to the above explanations. He states that by using a sufficiency of hydrochloric acid, calcium thiosulphate splits up completely into sulphurous acid, sulphur, water, and calcium chloride. It is of course supposed that boiling is not undertaken until the reaction is over; the sulphurous acid absorbed by the liquid will thus be expelled completely.

Stahlschmidt agrees with Mond's views to a certain extent, but mentions that in Schaffner's method large quantities of gypsum are formed, which seems to indicate that the quantity of sulphurous acid is too large; the oxidised residues are probably specially rich in thiosulphates, so that on the decomposition of the lyes by hydrochloric acid too much sulphurous acid is set free.

On account of these contradictory results, the author made it his object to investigate this subject. A very complete series of trials was made, and the results obtained proved that Stahlschmidt and Schaffner's accounts were perfectly trustworthy. The formation of trithionic acid only takes place in cases of incomplete saturation with hydrochloric acid, a circumstance which is not likely to occur with Schaffner's apparatus. The following figures are the number of grams in 1 litre of the lye used for experimenting. The specific gravity at 15° was 1·065:—

5·440	sulphur as sulphuric hydrate	32	equal to	1·70 eq. base
8·208	„ sulphide „	16	„	5·13 „
1·653	„ sulphate „	16	„	1·03 „
16·064	„ thiosulphate „	32	„	5·02 „
31·365				12·88
25·430	lime	28	equal to	9·08 eq. sulphur
12·896	soda	31	„	4·16 „
38·326				13·24

D. B.

Denitrating Action of the Glover Tower. By G. LUNGE (*Dingl. polyt. J.*, ccxxviii, 152—160).—The author in this, his concluding paper, strongly criticises a paper by Hurter (*Dingl.*, ccxxvii, 563) on the same subject. He asserts that the result of all experiments made by methods not affected by errors through sulphurous anhydride or nitric peroxide, is that there is no appreciable loss by denitration (1.) Hurter's attempt to upset the author's computation of Vorster's results is a failure; and his own assignment of all or most of the non-"mechanical" loss to the Glover tower is entirely without foundation. (2.) Although Hurter asserts in various places that he agrees with Vorster's results, the contrary is the case; for (*a*) Vorster makes the loss in the Glover tower 67·9 per cent., and even 94 per cent. of the nitre in circulation; Hurter makes it only "the greater half" of 22 per cent. (*b*) Vorster asserts that only nitrogen is produced, and no nitrous oxide at all; Hurter speaks it only of nitrous oxide. (*c*) Vorster declares the Glover tower to be unsuitable for the denitration of nitrose, and prefers the dilution method; Hurter says nothing of this, but admits that with the Glover tower less nitre is used than with the dilution method. (3.) The value of the author's denitration experiments, which was questioned by Hurter, is proved (*a*) by a refutation of Hurter's objection, (*b*) by new experiments in which all sources of error were eliminated. (4.) In Hurter's own experiments, the use of an alkaline absorption solution introduces a source of error. (5.) It is proved, contrary to Hurter's assertion, that when air and nitrogen dioxide are passed through sulphuric acid N_2O_3 only is formed, as Winkler has already shown. J. T.

Bottle-glass. By H. MACAGNO (*Chem. News.*, xxxviii, 5).—The following table gives the mean results of a number of analyses of bottle-glass. The solubility in water was obtained by weighing the quantity of material dissolved by 5 litres of water in one hour from 100 grams of finely-pulverised glass; the corrosion-degree was ascertained by boiling 100 grams of the same powder for one hour with 5 litres of potassium bitartrate solution of 0·33 per cent., and estimating the quantity of tartaric acid neutralised :—

	Spec. grav.	Chem. comp. per cent.				Solubility in water.	Corrosion degree.
		K_2O + Na_2O.	CaO.	Al_2O_3 + Fe_2O_3.	SiO_2.		
White glass (five samples)	2·453	14·51	8·22	1·92	75·34	2·617	2·020
Clear green glass (three samples)	2·474	15·52	7·73	5·47	71·27	3·177	3·975
Common green glass (eleven samples	2·570	10·92	15·10	10·34	63·56	2·600	3·202
Deep green glass (two samples).	2·674	3·38	26·58	10·53	58·59	1·270	1·275
Red-brown glass (six samples)..	2·516	15·77	9·28	6·88	66·15	3·470	4·888
Yellow-brown glass (seven samples)	2·553	14·62	14·35	8·02	62·84	2·504	3·387

One specimen of red-brown glass contained a trace of manganese. All the samples contained magnesia; in the analyses it is, when in sufficient quantity to be estimated, included with the lime. It would seem from the table that the chemical composition of glass is no criterion for judging of its quality. The amount of base does not indicate the resisting power to water or acids. The deep-green glass seems the best for wine-bottles, the clear-green, red-brown, and yellow-brown glasses are the worst, being easily attacked by solution of potassium bitartrate. C. W. W.

Glass with Alkaline Bases only. By P. EBELL (continued, see this volume, p. 689) (*Dingl. polyt. J.*, ccxxviii, 160—166).—3. *Behaviour of Silica towards Potassium Carbonate at the Fusing Point.*—200 parts of carbonate were heated with 100 parts silica in a platinum crucible. The fused mass was weighed directly to ascertain the amount of carbonic anhydride expelled; the amount of silica, alkali, and residual carbonic anhydride was also determined.

The fused mass gave :—

CO_2	2·96
SiO_2	39·86
K_2O	54·06
Moisture	3·12
	100·00

Abstracting the amount of potash required to combine with the carbonic anhydride, the rest gives ;—alkali : silica = 1 equiv. : 1·32 equiv. ; hence 1·32 eq. SiO_2 has expelled 1 equiv. CO_2.

The ratio of potash to silica obtained by direct weighing was 1 equiv. : 1·23, which is near to the previous one.

A series of fusions was made in which fresh equal portions of silica were added successively to the same carbonate. The first addition of silica was taken up with much more difficulty than the subsequent ones. So long as there was a considerable excess of undecomposed carbonate, white crystalline portions were clearly seen to separate from the well-fused mass on cooling. As the silica increased in amount this ceased. The crystals seem to be due to potassium carbonate which has been dissolved.

Five fusions were made in this series with the result that 1 equiv. SiO_2 added expelled 1·003, 0·851, 0·819, 0·782, 0·558 equiv. CO_2. The amount of carbonic anhydride expelled is therefore dependent on the relative quantities of silica and carbonate present.

4. *Behaviour of Soluble Glass in Aqueous Solution.*—A concentrated aqueous solution of potassium silicate was precipitated by alcohol; the precipitate and mother-liquor were analysed; the precipitate was dissolved and re-precipitated, and so on until three precipitates had been obtained. By each precipitation some potash was removed, so that the precipitate became continually richer in silica, until at last it ceased to be soluble in water.

5. *Dialysis of Soluble Glass through Parchment-paper.*—A not too concentrated solution gradually became richer in silica from the pro-

portion $SiO_2 : K_2 = 2·73$ equiv. : 1 equiv., to the proportion $SiO_2 : K_2O = 7·79$ equiv. : 1 equiv. Some silica passed through the paper in combination with the alkali.

6. *The Sulphur Reaction with Soluble Glass in the Wet Way.*—A solution of sodium silicate was digested with precipitated hydrated silica and filtered. A portion of the filtrate boiled with sulphur gave no reaction with lead acetate. By the gradual addition of caustic soda and continual testing with sulphur and lead acetate, a reaction with the lead was ultimately obtained. The sodium silicate formed then gave on analysis the proportion $SiO_2 : Na_2O = 2·1$ equiv. : 1 equiv. Since a little caustic soda must have been in excess the limiting relation will not be very far from that previously obtained in the dry way, viz., $2·5\ SiO_2 : 1$ base. This, then, appears to correspond to a really neutral soluble glass. J. T.

Influence of Light on Cement. (*Dingl. polyt. J.*, ccxxviii, 277—278.)—The following trials were made by Heintzel. Three samples of the same cement were preserved in various ways, A in the air with full light, B in the air with diffused light, C in the dark with but little access of air. After the lapse of six months the following differences were observed:—

Sample.	Loss by ignition.	Time for setting.	Firmness for 1 sq. cent.		Colour.	Remarks.
			After 28 days.	After 7 days.		
	p. c.		k for 1 sq. cent.			
A.	7·6	?	2·2	3·0	Pale yellow	Required 38 p. c. of its weight of water for making into mortar; had become lumpy.
B.	3·5	3 hours	21·4	37·9	Grey with yellow tinge	After adding 33·3 p. c. of water it was difficult to work it with a trowel; does not expel any water.
C.	1·5	6 hours	31·6	44·6	Grey with blue tinge	Requires 33·3 p.c. of water; expels water.

Heintzel concludes from these differences, that it would be profitable to store cement in a loose state in the dark. The changes of colour are explained by the fact that the iron compounds are transformed into oxidation-products due to the action of light in presence of air. Dyckerhoff, Delbrück, and Lieven undertook some experiments in this direction, but did not arrive at the same conclusion, the latter chemist stating that it is almost impossible that light could penetrate through cement. D. B.

Condensation of Zinc-vapours in the Blast-furnace. By A. LENCAUCHEZ (*Dingl. polyt. J.*, ccxxviii, 267—271).—This paper describes the results of some experiments made by the author and Müller in 1877. The question of obtaining zinc in blast-furnaces having reappeared, the author thought it of interest to give an account of the results of his experiments:—

1. *Tension of Zinc-vapour.*—Even at very high temperatures the tension of zinc-vapour was not much more than the pressure of the atmosphere.

2. *Oxidation of Zinc-vapours by Carbonic Acid.*—Zinc-vapour is converted into the oxide, and the carbon dioxide reduced to monoxide at a temperature of 400°.

3. A sublimation of zinc oxide takes place by treatment with carbonic oxide.

4. *Zinc-dust or Zinc-grey.*—This substance consists of metallic zinc containing 4 to 8 per cent. of oxide, also ferric oxide, plumbic oxide, ash, charcoal, and other oxides present in the ore.

5. *Reduction of Oxide of Zinc by Blast-furnace Gases.*—This reduction takes place at a white heat, but at a lower temperature the metal is again oxidised by the carbonic acid.

6. By mixing finely-powdered zinc sulphide with other metallic sulphides (lead sulphide) in a crucible and adding powdered charcoal, clay, and lime, and heating to a white heat, a violent evolution of zinc-vapour and carbon sulphide takes place, whilst lead sulphide remains behind. In an open vessel, carbonic and sulphurous acids and zinc oxide are obtained. Under 500° a result similar to that in experiment (3) was obtained.

7. *Oxidation of Zinc-vapours by the Gases from Zinc Blast-furnaces.*—The results in experiments (2) and (3) showed that carbonic acid oxidises melted zinc or zinc-vapours, whilst carbonic oxide reduces zinc oxide only at temperatures above 1200°. Carbonic acid coming in contact with zinc-vapours at a temperature lower than 1200°, oxidises the latter very readily. This oxidising power, which carbonic acid seems to possess when passed over melted zinc, proved to be a very characteristic test of its presence, as a mixture of gases containing only 0·5 per cent. of this gas was perfectly freed from it by being passed, along with zinc-vapour, through a tube heated to whiteness.

8. *Condensation of Zinc-vapours.*—An apparatus is described by which it is possible to cool zinc-vapour (reduced by carbonic oxide at a temperature of 1200°) to 300° in one-third of a second. In this way about 5 to 7 per cent. of zinc-vapour only is oxidised, the remainder being condensed.

9. *Agglomeration and Melting of Zinc-dust.*—The preparation of metallic zinc is always accompanied by the formation of zinc-dust. The latter forms a metallic, very porous and light powder; its density being scarcely 1. It burns very readily, and is oxidised when exposed to the air for a few days. By condensation it assumes the properties of metallic zinc. By hydraulic pressure it acquires a sp. gr. of 6. Bricks made from zinc-dust by pressure are oxidised very gradually. A specimen of 70 mm. in thickness was oxidised completely after six months' exposure to the atmosphere. It is an interesting fact that these zinc-agglomerates melt at the same temperature as metallic zinc, without absorbing foreign substances; their volume decreases con-

tinually, and finally a residue of the form and thickness of a lead-pencil is left. The latter is composed of the impurities present in zinc-dust. This melting effects a purification, the product obtained being equal to pure refined zinc.

The above results show, that (1) a zinc blast-furnace can only be used when a cheap ore containing much iron and but little zinc is to be worked up; (2) that ores consisting of galena and zinc-blende may be worked up in cupola-furnaces; and that (3) zinc-dust agglomerates profitably and may be used for the direct preparation of pure zinc.

D. B.

Influence of Impurities on the Desilvering of Lead. By C. KIRCHOFF (*Dingl. polyt. J.*, ccxxviii, 265—267).—The fact that it is necessary to refine hard raw lead previous to the addition of zinc is not mentioned in metallurgical works, although the difficulties which present themselves when lead is freed from silver in the presence of impurities have been long known. An attempt to desilverise raw lead, and thus after refining to obtain a hard lead free from silver, gave the following results:—

	I. Not refined.			II. Refined.		
	Contents of silver in 1 ton.	Zinc charges.		Contents of silver in 1 ton.	Zinc charges.	
		No.	Weight.		No.	Weight.
	g.		k.	g.		k.
Before adding zinc......	2662·93	—	—	2952·24	—	
After the 1st charge....	2659·82	1	113·40	2662·93	1	68·54
" 2nd "	2653·60	2	113·40	1480·78	2	68·54
" 3rd "	2606·93	3	68·54	500·85	3	68·54
" 4th "	2597·60	4	45·36	52·88	4	68·54
" 5th "	2582·00	5	45·36	5·60	5	45·36
" 6th "	14·9945	6	45·36	—	—	—
" 7th "	225·10	7	45·36	—	—	—
" 8th "	24·89	8	31·84	—	—	—
" 9th "	4·6	9	13·61	—	—	—
			522·23			319·52

The amount of zinc used in (I) was 2·87 per cent.; in (II) only 1·75, while the time of operation, labour, and fuel were reduced to one-half. (I) gave 43 per cent. of refined lead; while in (II) 72 per cent. were obtained; this includes loss of refining products. It is shown, therefore, that elimination of silver without previous refining of lead can be undertaken only when the latter contains but a small percentage of impurities.

D. B.

Burning of Bricks in Annular Kilns. (Continued from page 69. *Dingl. polyt. J.*, ccxxviii, 69.) By F. FISHER (*Dingl. polyt. J.*, ccxxviii, 242—249).—In the second part of this paper the author compares

Clay from	Under 900 to 1000° (melting of brass).	1000 to 1100° (melting of silver).	1100 to 1200° (melting of copper).	1200 to 1400° (cast-iron melted).	1400 to 1600° (melting of steel).	1600° and over (wrought-iron melted).
I. Gneppin....	F. Unaltered. S. Dull; porous. Fr. Earthy, hard, whitish yellow.	Scarcely altered.	F. Unaltered. S. Dull, yellowish brown. Fr. Almost perfectly close. E. Slightly translucent.	As before, but of a more dark red colour.	F. Nearly retained. S. Grey, brown lustre, warty. Fr. Fine pores. E. Not translucent.	F. Recognisable, but swelled up strongly. E. Round.
II. Liegnitz...	F. Unaltered. S. Dull; very porous. Fr. Not as hard as former, earthy.	Scarcely altered.	F. Unaltered. S. Dull. Fr. Earthy, strongly absorbent, yellowish white.	F. Retained. S. Dull, grey. Fr. Porous, granular. E. Not translucent.	F. Slightly swelled and distorted. S. Slightly vitrified. Fr. Like sugar. E. Round.	F. Opened to a frothy mass. E. Quite disappeared.
III. Kottiken..	F. Unaltered. S. Dull, porous. Fr. Earthy, firm, whitish yellow.	Scarcely altered.	F. Unaltered. S. Dull, white yellow. Fr. Earthy, absorbent. E. Not translucent.	F. Retained. S. Dull, whitish yellow. Fr. Closed, scarcely absorbent. E. But little translucent.	F. Retained. S. Scarcely shiny. Fr. Quite close. E. But little translucent.	F. Quite retained. Fr. Somewhat porous. S. Slightly vitrified.
IV. Ledetz....	F. Unaltered. S. Dull, porous. Fr. Earthy, firm, whitish yellow.	Scarcely altered.	F. Retained. S. Light. Fr. Perfectly close. E. Slightly translucent.	F. Slightly swelled up. S. Vitrified, warty. Fr. Fine holes. E. Very round.	Swelled up to a frothy slag with large holes.	Spread out in the form of a grey enamel.

Clay from	Under 900 to 1000° (melting of brass).	1000 to 1100° (melting of silver).	1100 to 1200° (melting of copper).	1200 to 1400° (cast-iron melted).	1400 to 1600° (melting of steel).	1600 and over (wrought-iron melted).
V. Rathenow..	F. Unaltered. S. Dull, strongly absorbent. Fr. Earthy, firm, brick red.	Scarcely altered. More of a dark red colour.	F. Swelled. S. Slightly vitrified. Fr. Brownish red, frothy. E. Completely round.			
VI. (Clinker) Bockhorn	S. Unaltered. S. Dull, strongly absorbent. Fr. Earthy, firm, brick red.	Scarcely altered. More of a dark red colour.	F. Retained. S. Slightly vitrified. Fr. Quite close, reddish brown, shiny.	Forming brown enamel.		
VII. (Clinker) Schwarzhütte	S. Unaltered, very porous. Fr. Earthy, united but very little, brick red.	Scarcely altered. More of a dark red colour.	F. Quite retained. S. Dull. Fr. Almost close, reddish brown, but little shiny.	F. Much distorted. S. Vitrified. Fr. Frothy. E. Perfectly round.		
VIII. Christiana	F. Unaltered, porous. Fr. Earthy, firm, flesh red colour.	F. Unaltered. S. Dull. Fr. Almost close, reddish brown.	Melted to a large blistery frothy globule.			

Abbreviations :—F. = Form.
S. = Surface.
Fr. = Fracture.
E. = Edge.

Bischof's, Seger's, and Richter's methods, their laws and theories, respecting the relation between fusibility and chemical composition of clays. A long discussion follows, and it is shown that the abovenamed methods give only approximate numbers for the fusing points of clays, as various substances present in kaolins interfere with the results obtained. Seger made some fusion tests which seemed to show that the degree at which slagging, and finally softening of kaolins take place depends chiefly on the substances of which the clay is composed, and that their resistance is influenced largely by the quantities of felspar and quartz present. Kaolins exposed to a very high temperature retain their consistency, provided that they are almost free from felspar, and that the substances which form the clay are constant to heat. The following qualities were investigated more fully, their composition having been given in the first portion of this paper. The results may be tabulated as follows (see pp. 762—763):—

In conclusion of the second part of this paper, the author describes some experiments which were undertaken in annular kilns. The results cannot be understood without the drawing attached to the paper. D. B.

On the Fatty Matter of Vateria Indica, or Piney Tallow.

By G. DAL SIE (*Gazzetta chimica italiana*, viii, 107—119).—The two samples of this vegetable tallow examined by the author, the one obtained from Venice, the other from Trieste, differed somewhat in appearance, one being more carefully prepared than the other. The fat is obtained from a copaliferous tree, the *Vateria indica*, growing in Malabar. A careful examination, of which full details are given, showed that this substance consists of a mixture of free palmitic acid, (75 per cent.), and free oleic acid (22·8 per cent.), besides a small quantity of impurity, which may be separated by filtration of the fused mass. The presence of volatile acids or glycerin could not be detected.

The crude fat may be bleached, after filtration, by mixing it with an equal bulk of boiling water, adding 9 per cent. of nitric acid, and boiling for a few minutes. In this way the greenish colour of the original substance is changed to yellow, and a subsequent exposure to the sun and air, after the acid has been removed by washing with boiling water, easily completes the bleaching process. At the same time the melting point of the fat is raised. In this form it makes good candles which give a brilliant light. The palmitic and oleic acids may also be separated by pressing in the usual way previous to bleaching. Other methods of bleaching, such as potassium dichromate, hypochlorites, &c., did not yield satisfactory results. C. E. G.

General and Physical Chemistry.

Thermic Researches on the Chromates. By F. MORGES (*Compt. rend.*, lxxxvi, 1443—1446).—The heat of combination of chromic anhydride with water, as represented by the equation, $CrO_3 + H_2O = CrO_4H_2$, is 580, and the paper gives the heat disengaged by successive additions of water in single molecules. The curve representing this shows a minimum at $CrO_4H_2, 4H_2O$, so that there appears to be a definite hydrate of chromic acid of this formula.

The heat of combination of chromic acid with alkaline hydrates was determined by the author, the amount of alkali required to saturate the acid being added by halves. The results at 19·5° were the following:—

	HKO.	$HNaO$.	HNH_4O.
First half of alkali....	6,246	6,519	6,747
Second half of alkali ..	5,123	5,316	5,463
Total..........	11,369	11,835	12,210

The numbers for sodium agree closely with those of Thomsen, namely, 6,567 and 5,793.
R. R.

Thermo-chemistry. Function of Auxiliary Acids in Etherification. By BERTHELOT (*Compt. rend.*, lxxxvi, 1296—1302).—As example of etherification, the author has taken the production of acetic ether from alcohol and acetic acid by aid of hydrochloric acid. In order to investigate this subject, the amounts of heat developed in the production of the various compounds, resulting from the reciprocal action of alcohol, water, hydrochloric acid, acetic acid, and the ethers of these acids, were determined. These results are tabulated below.

I. Compounds with hydrochloric acid (gas).

(2.) Hydrates:

To form $HCl + 2H_2O$, + 11·6 heat-units* are disengaged.
„ $HCl + 6·5H_2O$, + 14·0 „ „
„ $HCl + H_2O$ in excess, 17·4 „ „

(2.) Alcoholates:

$HCl + 1·15\ C_2H_6O$ at 12°, + 10·8 units are disengaged.
$HCl + 1·59\ C_2H_6O$ „ + 11·5 „ „
$HCl + 300\ C_2H_6O$ „ + 17·35 „ „
$\left\{\begin{array}{l} HCl + C_2H_6O \\ HCl + 3C_2H_6O \end{array}\right.$ „ + 10·6 „ „ / „ + 13·8 „ „

The last two results are obtained from the others by interpolation.

(3.) With acetic acid:

In forming $HCl + 5·8C_2H_4O_2$ at 13°, + 6·22 units are disengaged.
„ $HCl + 41C_2H_4O_2$ „ + 7·1 „ „
„ $HCl + 200C_2H_4O_2$ at 16°, + 7·09 „ „

---

* Kilogram-degrees.

(4.) With acetic ether:

In forming $HCl + 1\cdot36C_2H_5(C_2H_3O_2)$, + 8·82 units are disengaged.
„ $HCl + 2\cdot64C_2H_5(C_2H_3O_2)$, + 9·82 „ „
„ $HCl + 11\cdot84C_2H_5(C_2H_3O_2)$, + 11·84 „ „

(5.) Hydrochloric acid is scarcely absorbed by ethyl chloride.

II. Compounds with acetic acid.

$C_2H_4O_2 + H_2O$ absorbs − 0·15 unit (Favre and Quaïllard).
$C_2H_4O_2$ and a large quantity of water at 7° produces + 0·40 units (Berthelot and Louguinine).
$C_2H_4O_2 + C_2H_6O$ at 12° absorbs − 0·06 units (about).
$2C_2H_4O_2 + C_2H_5(C_2H_3O_2)$ at 13° disengages + 0·26 units (about).
$1\cdot27C_2H_4O_2 + C_2H_5Cl$ „ „ + 0·02 „ „

III. Compounds with water.

Alcohol mixed with water at 12° disengages + 2·6 units.
Acetic ether mixed with water at 16° disengages + 3·1 units.
Ethyl chloride mixed with water at 16° disengages + 2·0 units (about.)

IV. Various compounds not mentioned above.

In forming $C_2H_6O + 0\cdot59C_2H_5(C_2H_3O_2)$ at 12° absorption of − 0·09 units (about).

In forming $1\cdot7C_2H_6O + C_2H_5(C_2H_3O_2)$ at 12° absorption of − 0·15 units (about).

In forming $1\cdot23C_2H_6O + C_2H_5Cl$ at 12° absorption of − 0·2 units (about).

In forming $1\cdot23C_2H_5Cl + C_2H_5(C_2H_3O_2)$ at 11·5° absorption of − 0·08 units (about).

In connection with the action of hydrochloric acid upon acetic acid, the author points out that the formation of acetyl chloride by the direct union of these bodies would produce an absorption of 12·6 heat-units, showing why this reaction does not take place, but rather the inverse one.

$$C_2H_3OCl + H_2O = C_2H_4O_2 + HCl \text{ (gas)}.$$

This reaction disengages + 5·5 units. Further, to form acetyl chloride in the above manner, the presence of some body is needed, which by its union with water would produce an amount of heat greater than + 5·5 units. Such an one is phosphoric anhydride; but neither alcohol nor water, nor a mixture of the two, can supply the required amount of energy, so that acetyl chloride cannot be formed from hydrochloric acid and acetic acid in the presence of water or alcohol. Therefore, the theory, recently proposed, which supposes this to take place as a stage in the etherification of acetic acid, is not tenable.

From the data given above, the production of acetic ether from alcohol, acetic and hydrochloric acids would take place in the following way:—

(1.) C_2H_6O (liq.) + $C_2H_4O_2$ (liq.) = $C_2H_5(C_2H_4O_2)$ + H_2O absorbs	− 2·0 units
Solution of acetic ether in excess of alcohol absorbs	− 0·1 ,,
,, water ,, ,, disengages	+ 0·3 ,,
,, HCl (gas) ,, ,, ,,	+17·4 ,,
Total effect..	+ 15·0 ,,

(2.) Formation of an equivalent of ethyl chloride.

C_2H_6O (liq.) + HCl (gas) = C_2H_5Cl (liq.) + H_2O (liq.) produces	+ 3·4 units
Solution of ethyl chloride in alcohol absorbs ..	− 0·3 ,,
,, of water in excess of alcohol disengages	+ 0·3 ,,
,, of $C_2H_4O_2$ (liq.) ,, absorbs..	− 0·1 ,,
Total effect..	+ 3·3 ,,

The first reaction disengages + 11·7 units more than the second; this excess is chiefly due to the production of the alcohol hydrochloride.

If water is excluded, as in the production of acetic ether from alcohol and acetyl chloride by the direct union of these bodies, + 19·3 units are disengaged, whilst the formation of ethyl chloride gives rise to + 7·1. Thus in this case also the first reaction disengages + 12·2 units more than the second.

If an excess of water be present instead of an excess of alcohol, the following results are obtained :—

(1.) Formation of an equivalent of acetic ether produces an absorption	− 2·0 units
Solution of acetic ether in water produces ..	+ 3·1 ,,
,, of HCl (gas) ,, ,, ..	+17·4 ,,
Total effect..	+18·5 ,,

(2.) Formation of an equivalent of ethyl chloride produces	+ 3·4 units
Solution of ethyl chloride in water produces ..	+ 2·0 ,,
,, of $C_2H_4O_2$ in water ,, ..	+ 0·4 ,,
Total effect..	+ 5·8 ,,

Here again the first reaction produces + 12·7 units more than the second, this excess being due chiefly to the production of the hydrate of hydrochloric acid. These results apply only to low temperatures: at 100° or above, the dissociation of the hydrochlorates of water and alcohol diminishes their effect, so that the reverse action takes place at these temperatures, viz., the production of ethyl chloride.

The author concludes that the explanation of the function of the auxiliary acids is to be sought in the amount of heat produced by their combining with alcohol or water, the heat thus disengaged increasing the chemical action. Similarly, the difference between the rate of production of acetic and nitric ether is to be found in the different amounts of heat developed in mixing the acids with alcohol. Thus acetic acid absorbs 2 units when mixed with alcohol, and production of its ether takes place slowly, whilst nitric acid under similar circumstances develops + 6·2 units, its ether being formed instantaneously. From the difference between these numbers, the author concluded that nitric acid might be used to accelerate the process of etherification, and this he verified by experiment in the case of acetic acid.

Similarly the formation of nitro-compounds, by the action of a mixture of nitric acid and sulphuric acids, *e.g.*, on benzene, takes place in preference to the formation of sulpho-compounds, since the heat developed in the former case is greater than that produced in the latter.

P. P. B.

Thermo-chemistry of some Substituted Acetic and Benzoic Acids. By W. LOUGUININE (*Compt. rend.*, lxxxvi, 1329—1332).—The author finds that the substitution of chlorine for hydrogen in acetic acid raises the amount of heat disengaged when the acid combines with soda. In state of solution, however, no regularity in the increase is exhibited, since monochloracetic acid disengages in this reaction 14·398 heat-units,* whilst trichloracetic gives 14·056. It would thus appear that monochloracetic develops more heat than trichloracetic in combining with soda, when in solution; but on the formation of sodium trichloracetate, calculated for the solid state, 26·448 units are disengaged, whilst in the formation of sodic acetate only 18·3 units (Berthelot) are disengaged, thus showing that trichloracetic acid is a stronger acid than acetic acid.

Experiments made with glycocine and alanine show that the substitution of NH_2 for hydrogen has a neutralising tendency. These bodies exhibit but little energy in combining with bases or hydrochloric acid, still the amount of heat developed in combining with soda is always greater than that formed by combination with hydrochloric acid.

From the following table, which gives the amounts of heat developed in the formation of sodium benzoate, nitrobenzoate and amidobenzoate, it will be seen that the nitro-group has a great influence on the amount of heat developed, whilst the NH_2 group diminishes the heat developed; it has not, however, the same influence as in the fatty series, for whilst by its substitution in the fatty acid a weak acid is formed, which the author compares to hydrocyanic acid, in those of benzoic acid, an acid is formed comparable with carbonic and boric acids. This analogy resembles that of the fatty alcohols and phenols with regard to the amounts of heat developed by union with bases.

			Acid.		
Acid.	Base.	Salt.	Nitrobenzoic.	Benzoic.	Meta-amido-benzoic. (m. p. 172°).
			Heat-units.	Heat-units.	Heat-units.
Dissolved.	Dissolved.	Dissolved.	+ 12·804	+ 13·5	+ 9·27
Solid.	ditto.	ditto.	+ 7·710	+ 7·0	+ 5·11
Dissolved.	ditto.	solid.	+ 14·074	+ 12·7	+ 7·874
Solid.	ditto.	ditto.	+ 8·980	+ 6·2	+ 3·725
All separated from water.			+ 18·720	+ 16·0	+ 13·509

P. P. B.

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* Kilogram-degrees.

Rock Crystal Weights and Measures. By H. BUFF (*Deut. Chem. Ges. Ber.*, xi, 1076—1078).—The author does not consider that rock crystal is a more suitable material than platinum for the standards of weight and lineal measure. W. C. W.

Law of Volumes. By H. SCHRÖDER (*Deut. Chem. Ges. Ber.*, xi, 1109—1111).—Every solid compound contains one element whose *stere* or volume measure exerts a dominating influence over the other components, assimilating their steres to its own. A solid molecule contains whole volumes or steres of its component elements, but never fractions. If the atomic weights are expressed in grams, the steres represent cubic centimetres, *e.g.*, $\overline{\mathrm{Ag}\tfrac{2}{1}}\mathrm{Cl}\tfrac{3}{1} = 5 \times 5{\cdot}14 = 25{\cdot}7$; *i.e.*, 143·5 grams of silver chloride occupy 25·7 cubic centimetres, or five silver steres. The dash over Ag indicates that in silver chloride, silver is the predominating stere; the numbers above the line show the number of steres in the compound, thus : silver chloride occupies $2 + 3 = 5$ steres, and the figures below the line express the number of atoms of the respective elements in the compound. The author has verified this law for three groups of minerals, viz. :—

α. Silicon, quartz, sillimanite and disthene. β. Aluminium, corundum, chrysoberyl, diaspore, and andalusite. γ. Magnesium, periclase, spinelle, olivine, diopside, humite, and garnets. W. C. W.

Law of Volumes. By H. SCHRÖDER (*Deut. Chem. Ges. Ber.*, xi, 1111—1116).—The author gives the molecular volumes of a large number of mercury compounds and of the oxides and silicates of manganese. In crystalline red mercuric sulphide, the sulphur stere, 5·3, predominates, the molecular volume of this compound being 29·1 ($\mathrm{Hg}\tfrac{5}{2}\,\overline{\mathrm{S}\tfrac{6}{2}} = 11 \times 5{\cdot}3 = 58{\cdot}3 = 2 \times 29{\cdot}1$), but in black amorphous mercuric sulphide and in most other mercuric compounds the mercury stere, 5·52, predominates, *e.g.*, $\overline{\mathrm{Hg}\tfrac{5}{2}}\,\mathrm{S}\tfrac{6}{2} = 11 \times 5{\cdot}52 = 60{\cdot}72 = 2 \times 30{\cdot}36$. W. C. W.

Inorganic Chemistry.

Spontaneous Ignition of Hydrogen by Finely Divided Zinc. By P. W. HOFMANN (*Chem. Centr.*, 1878, 351).—The author noticed some explosions during the preparation of chloride of zinc by dissolving the metal in hydrochloric acid. He explains this circumstance in the following manner. The hydrogen gas evolved in large quantities throws up portions of zinc (which have become very porous through the action of the acid) to the surface of the liquid, in which case the finely divided metal is brought into contact with the air and the hydrogen, and causes the explosion of the gaseous mixture in a manner similar to spongy platinum. Schering has noticed the same phenomenon at his works in Berlin without giving any satisfactory explanation. In his factory the solution of large quantities of zinc in dilute acid is effected in open vessels, which are provided with iron covers. When ignition of the gas takes place, the covers are placed over the dissolving vessels, and thus the flame is extinguished. D. B.

Transparent Hydrated Silica and Hydrophane. By E. Monier (*Compt. rend.*, lxxxvi, 1318—1319).—In this memoir the author gives further details of the method of preparing these bodies by the long-continued action of a dilute solution of oxalic acid upon a solution of an alkaline silicate. For this purpose a solution of the silicate is brought into a vessel inclined at an angle of 45°; on to this a layer of a dilute oxalic acid is poured, and the whole is allowed to stand for some months: where the two liquids meet, a layer of transparent silica is formed, whilst below this and gradually filling the vessel layers of porous silica form.

The hydrated transparent silica scratches glass, contains much hygrometric water, which it loses at a low temperature (30—35°), becoming at the same time milky like opal, and of the same hardness; in this state it also retains 9—13 per cent. of water. Its density varies from 2·03—2·07, and it is singly refractive. Portions which have become opaque by exposure to air or by heating, become translucent when treated with water, thus resembling hydrophane. After exposure to a red heat, this hydrated silica possesses a mother-of-pearl lustre, is very brittle, exhibits cleavage in its longitudinal direction, and dissolves in a boiling concentrated solution of potash.

The gelatinous silica formed at the same time becomes, in the course of a few months, transparent and very hard, and possesses the properties of hydrophane.

Experiments of a similar nature are being made with salts of aluminium, of iron, &c. P. P. B.

Production of Sodium Carbonate by the Action of Magnesium Carbonate on Sodium Chloride. By S. Cloez (*Compt. rend.*, lxxxvi, 1446—1447).—In explanation of the origin of the deposits of sodium carbonate which occur near the salt lakes in the East and in warm countries, Berthollet suggested the action of calcium carbonate upon sodium chloride. This hypothesis is unsupported by experiment, and is indeed inconsistent with some well-known facts; but the author, on substituting for calcium carbonate a solution in which magnesium carbonate is dissolved by excess of carbonic acid, found that sodium bicarbonate is formed by reaction with a solution of sodium chloride at ordinary temperatures. In the residue left by the evaporation of the mixed solutions at ordinary temperatures, magnesium chloride and sodium bicarbonate were detected, and as the evaporation takes place under like conditions in nature, the experiment explains the production of sodium carbonate, and the large quantity of magnesium chloride which the waters of these lakes hold in solution. R. R.

Lime, Strontia, and Baryta in the Crystalline State. By G. Brügelmann (*Ann. Phys. Chem.* [2], iv, 277—283).—By heating the nitrates of barium, strontium, and calcium in covered porcelain crucibles placed in a coke fire, the author has succeeded in obtaining crystals of the oxides so much larger than those described in his former paper (*Chem. Soc. J.*, 1878, xxxiv, 471), that several other crystallographic and physical properties of the three oxides have been made out. The paper describes in detail the configuration and grouping of the crystals in each case. The sp. gr. of the crystals were found to be $CaO = 3·251$, $SrO = 4·750$, $BaO = 5·722$; and the specific volumes calculated from these results are $CaO = 17·225$, $SrO = 21·789$, $BaO = 26·739$. It may be noted that the sp. gr. and specific volume of strontia have very nearly the values of the means between those of lime and baryta. R. R.

Crystalline Zinc Oxide. By G. BRÜGELMANN (*Ann. Phys. Chem.* [2], iv, 283—286).—The author obtained oxide of zinc in microscopic crystals by the same process which yielded crystals of the alkaline earth oxides, viz., by heating the nitrate in a porcelain crucible. The crystals of zinc oxide form beautiful hemimorphous pyramids belonging to the hexagonal system. They are white or slightly yellow in colour, and have brilliant surfaces. The sp. gr. of zinc oxide in this condition is 5·782 at 15°, and the corresponding specific volume is 14·009. R. R.

Preparation of Violet Ultramarine. By ZELTNER (*Chem. Centr.*, 1878, 320).—The following methods depend upon the introduction of hydroxyl into ordinary ultramarine blues or greens:—(1.) Chlorine is passed over ultramarine at 300°, or ultramarine is treated with sulphuric anhydride and the mass warmed with water, with alkaline carbonates, or with caustic alkalis. (2.) The hydroxyl derivative is obtained directly by treating blue or green ultramarine with chlorine and steam at 160—180°. (3.) Mixtures of salts are used, which, when heated, split up into halogens, nitrogen, &c. By heating blue ultramarine with such mixtures, *e.g.*, with sodium nitrate and ammonium chloride in a crucible, violet-ultramarine hydroxide is at once obtained, respectively violet-ultramarinamide if ammonium salts are present. (4.) Blue ultramarine is exposed to the action of an acid at 160—180°, to an oxidizing agent, and water. (5.) A solution of calcium and magnesium chlorides is added to ultramarine, and the whole heated in a crucible. (6.) By the action of steam and nitric or hydrochloric acids on blue ultramarine. D. B.

Preparation of the Double Carbonate of Uranium and Ammonium, and Separation of Iron and Uranium. By E. BURCKER (*J. Pharm. Chim.* [4], xxvii, 347—349).—The double carbonate, $[(U_2O_2)O.CO_2]$, $[N_2H_8.O_2.C_2O_4]$, was first prepared by Péligot, and afterwards examined by Ebelmen (*Ann. Chim. Phys.* [3], 44 and 206). The author prepares it by the following process:—Solutions of uranium nitrate and ammonium sesquicarbonate containing free ammonium are mixed (ammonium sesquicarbonate 100, distilled water 400, and liquid ammonia 100 c.c.). The precipitate at first formed is dissolved in an excess of the ammonium mixture and then filtered.

The filtrate, when left to evaporate spontaneously, deposits the double carbonate in a short time. The composition of the crystals is the same as those prepared by Péligot and Ebelmen. When its aqueous solution is boiled it becomes turbid, and deposits yellow uranium hydrate, whilst ammonium carbonate is evolved. It is insoluble in alcohol and ether. The salt may also be prepared—like the double carbonate of uranium and potassium or sodium—by treating a uranium salt with an excess of a concentrated solution of ammonium sesquicarbonate without free ammonia, filtering, and leaving the solution at a temperature of 50—60°, when the yellow crystals gradually form.

In the separation of iron and uranium the author finds that the method based on the precipitation of the iron with ammonium carbonate cannot be relied on, as after a short time the double carbonate of uranium and ammonium is deposited, and it is almost impossible to free the iron precipitate from it. The following method was found to give good results—it is given by H. Rose in his *Traité d'Analyse Quantitative*:—The solution of iron and uranium as peroxides is precipitated with ammonia; the precipitate ignited and weighed, then reduced in a current of hydrogen; and the iron finally dissolved out with dilute hydrochloric acid, precipitated with ammonia, and weighed.

R. C. W.

Manufacture of Ferromanganese and Volatility of Manganese. By P. JORDAN (*Compt. rend.*, lxxxvi, 1374—1377).—By treatment of manganese ores in blast furnaces at St. Louis, near Marseilles, ferromanganese has been obtained containing as much as 87·4 per cent. of manganese, but when this amount is exceeded the alloy tarnishes on exposure to the air. An analysis of a sample is given which contained Mn, 84·96; Fe, 8·55; C, 5·70; Si, 0·66; S, 0·035; and P, 0·005.

Observations made at the above manufactory in the production of ferromanganese have made it very evident that manganese is volatile at the temperature of the furnaces. This conclusion has been further borne out by heating ferromanganese contained in a graphite crucible, in a furnace. The ferromanganese so treated was found to contain a smaller percentage of manganese, and the crucible was penetrated by oxide of manganese.

P. P. B.

Chrome-Steel. By BOUSSINGAULT (*Compt. rend.*, lxxxvi, 1303). —This is an abstract of a memoir which treats of the history of the discovery of chrome-steel and ferrochrome by Berthier in 1821, and of experiments showing that chromium does not by its union with pure iron produce a steel. An account is also given of the production of this compound, of its properties, and the methods of analysing it.

P. P. B.

Organic Chemistry.

Action of Aqueous Vapour on Hydrocarbons at a Red Heat. By J. COQUILLION (*Compt. rend.*, lxxxvi, 1197—1200).—Dry methane and ethylene are decomposed into carbon and hydrogen by passing over a red-hot spiral of palladium wire, twice the volume of the original gas being formed. In presence of moisture, the carbon of the hydrocarbon unites with the oxygen of the aqueous vapours, forming carbon monoxide, and hydrogen is liberated; the gaseous products in this case occupy four times the volume of the original gas, *e.g.*—

$$CH_4 + H_2O = CO + 3H_2.$$

When a hydrocarbon, mixed with a limited supply of oxygen, is passed over red-hot palladium, hydrogen, carbon monoxide and dioxide, and water are formed. The amount of carbon monoxide increases and the dioxide diminishes as the supply of oxygen is decreased.

By increasing the quantity of hydrocarbon the reaction may be made to take place in two stages—

1. $2CH_4 + 3O_2 = CO_2 + CO + H_2 + 3H_2O.$
2. $CH_4 + H_2O = CO + 3H_2.$

These experiments explain the action of aqueous vapour on hydrocarbons in the blast furnace. W. C. W.

New Method of Preparing Normal Dimethyl-ethylene. By LE BEL and GREENE (*Bull. Soc. Chim.* [2], xxix, 306—309).—The authors have obtained this substance from butylic alcohol in the following manner:—500 grams of zinc chloride were placed in a flask raised to a high temperature, and butylic alcohol was added drop by drop, the gas furnished by the reaction being passed through condensing tubes charged with H_2SO_4 mixed with half its volume of water, which retained the greater part of the isodimethyl-ethylene. On leaving this washer, but still containing some isodimethyl-ethylene, the gas was received into dry bromine which had been distilled fractionally at least four times. The mixed bromides were fractionated into three parts, distilling at 145—152°, 152—154°, and 154—160° respectively. The last formed three-fifths of the whole, scarcely anything remaining behind at 160°; so that ethyl-vinyl, whose bromide boils at 166°, is not formed in the reaction. The fraction boiling at 154—160° contains the bromide $CH_3.CHBr.CHBr.CH_3$ (boiling point 156°), but it is impossible to separate it completely from the bromide $CH_2Br.CBr(CH_3)_2$, which boils at 148°.

In order to obtain dimethyl-ethylene, $CH_3.CH{=}CH.CH_3$, in a pure state, the bromide was treated with sodium. The reaction is excessively violent and requires special precautions. The resulting gas was passed through a washer containing 1 vol. $H_2SO_4 + \frac{1}{2}$ vol. H_2O, and then into two large globes containing concentrated hydriodic acid, where it slowly formed secondary butylic iodide (boiling point 118—121°).

Two normal butylenes are known, dimethyl-ethylene and ethyl-vinyl, each forming the same iodide. It was interesting to ascertain whether these iodides would yield the butylenes from which they were prepared.

The dimethyl-ethylene bromide yielded an iodide boiling at 118—121°, and a bromide boiling at 156—158°.

The ethyl-vinyl bromide treated in the same way also gave an iodide boiling at 118—121°, which was subsequently converted into the bromide (boiling point 156—160°). The bromide boiling at 166° was not reproduced. F. J. L.

Action of Boron Fluoride on Certain Classes of Organic Compounds. By F. LANDOLPH (*Compt. rend.*, lxxxvi, 1463).—The author's experiments lead him to announce as a general law that boron fluoride combines in definite proportions, equivalent for equivalent, with aldehydes, acetones, and carbonyls. The combination is attended by a considerable disengagement of heat. Fluoboracetone is an orange-coloured liquid which boils at 130—140°. Fluoborethylene, $C_2H_3.BF_2$, is decomposed by water with formation of a liquor boiling at about 10°, and probably fluorethane, C_2H_5F.

R. R.

Formation of Melamine from Guanidine. By M. NENCKI (*J. pr. Chem.* [2], xvii, 235—237).—When guanidine carbonate is dissolved in a little hot water, mixed with an equal weight of phenol, and then heated on a water-bath, carbon dioxide escapes. If after the cessation of the escape of the carbon dioxide, the mixture is heated on a sand-bath, the temperature gradually rises with evaporation of water up to 140°, ammonia then begins to be given off, and this goes on up to the boiling point of phenol, but it is most convenient to heat it for half an hour at 160°. When the mass thus obtained is dissolved in hot water and filtered, melamine crystallises out on cooling.

This method of formation of melamine may be explained either by supposing that the guanidine passes into cyanamide, with evolution of ammonia, and that the latter becomes condensed to melamine, or that three molecules of guanidine pass directly into melamine—

$$[(NH_2)_2{=}C{=}NH]_3 = C_3N_6H_6 + 3NH_3.$$

This reaction would be perfectly analogous to the conversion of urea into cyanuric acid. The author has endeavoured, but unsuccessfully, to prepare a derivative of guanidine corresponding with biuret. A new sulphate of melamine has been obtained as follows:—When melamine is dissolved by warming it with dilute sulphuric acid in excess, a sulphate crystallises out on cooling in long needles of the composition $(C_3N_6H_6)_2SO_4H_2 + 2H_2O$. If this salt is dissolved in the necessary quantity of warm sulphuric acid diluted with two to four times its bulk of water, short well-formed rhombic prisms of an acid salt are obtained which consists of $C_3N_6H_6SO_4H_2$. This salt is decomposed by water and passes into the neutral one. G. T. A.

Boron Compounds. By C. COUNCLER (*Deut. Chem. Ges. Ber.*, xi, 1106—1109).—*Ethylene borate*, $B(O.C_2H_4.OH)_3$, is formed by passing gaseous boron chloride through ethylene glycol; the reaction is completed by adding excess of liquid boron chloride. The borate is insoluble in absolute ether, but it dissolves slowly in chloroform. From this solution it is deposited as a yellowish-white crystalline mass, consisting of microscopic plates; it melts at 161·7°. Although it is incombustible, it imparts a green colour to a gas flame. It is decomposed by water or by moist air, forming boric acid and glycol.

Isopropyl borate, obtained by heating isopropyl alcohol and boric anhydride at 120°, is a mobile liquid, boiling at 140°. The difference between the boiling points of two boric ethers is three times the difference between the corresponding alcohols, *e.g.*, ethyl alcohol, b. p. 78°; normal propyl alcohol, 96·5°; difference = 18·5. Ethyl borate, 119°; normal propyl borate, 174·5°; difference $= 3 \times 18·5°$.

The product of the action of secondary octyl alcohol on boric anhydride decomposes on distillation *in vacuo* or in hydrogen. When distilled in air, it splits up into methylhexylketone and boric anhydride.

Boroxytrichloride, $BOCl_3$, obtained as a bye-product in the preparation of boron chloride, is a yellowish-green liquid, which decomposes on heating into boric chloride, chlorine, and boric anhydride. With water it forms boric and hydrochloric acids and chlorine.

W. C. W.

Glycollide. By J. H. NORTON and J. TCHERNIAK (*Compt. rend.*, lxxxvi, 1332—1335).—The authors find that the unsatisfactory yield and the impurity of glycollide obtained by Kekulé's method, viz., by heating potassium chloracetate, is to be explained by the fact that the chloracetate retains some water of crystallisation, which afterwards hydrates the glycollide, and thus forms glycollic acid. To obtain a completely anhydrous salt, an alcoholic solution of chloracetic acid is added to a solution of sodium in 15 times its weight of dry alcohol; the anhydrous chloracetate separates out as a white precipitate, which, after being pressed and dried at 100°, is gradually heated to 150°, and kept at that temperature for some time (two days). The product is freed from potassium chloride by boiling and washing with water. Glycollide so obtained is a light white powder, possessing an insipid taste, and does not redden blue litmus paper. It melts at 220° (Dessaignes gave 180°). Hot nitrobenzene dissolves a small quantity, which is deposited on cooling.

Ethylamine reacts with glycollide to form glycol-ethylamine, identical with the body obtained by the action of ethylamine on glycollic ether (Heintz).

Glycol-phenylamine is obtained by dissolving glycollide in aniline heated to 130°, and purifying the product by crystallisation from hot water. On cooling, it separates in tufts of long prismatic needles, which melt at 108°. By the spontaneous evaporation of the aqueous solution, it is obtained in large clino-rhombic prisms, which melt at 92°. The composition of glycol-phenylamine is expressed by the formula, $C_6H_5.NH.CO.CH_2.OH$. Alcohol, ether, chloroform, &c., dissolve it easily. It dissolves silver oxide, and is decomposed by potash into aniline and potassium glycollate.

In a foot-note the authors state that they have, without success, attempted to obtain glyconitril from glycollamide. They also recommend, as a substitute for phosphoric anhydride in such reactions, the use of quick-lime, which they find gives a better yield. P. P. B.

Decomposition of Propyl-glycol at High Temperatures. By E. LINNEMANN (*Liebig's Annalen*, cxcii, 61—65).—The author has previously shown (*Annalen*, clxi, 58) that monobromo- and monochloropropylene, as well as propylene bromide, at high temperatures in presence of water, gives acetone, whilst propylene chloride gives in addition propaldehyde. Nevolé (*Compt. rend.*, July 17, 1876) has also proved that isobutyl-glycol by similar treatment gives isobutylaldehyde. The author now finds that propyl-glycol, when dissolved in 20 times its weight of water and heated with a trace of hydrochloric acid in sealed tubes for two hours at 215—220°, is partially decomposed, nothing but propaldehyde being formed. Thus:— $CH_3.CH(OH).CH_2.OH = CH_3.CH_2.COH + H_2O$.

This decomposition depends to a very great extent on the amount of pressure in the tubes. The best results were obtained with tubes 25 centimeters long and 1 centimeter wide, filled two-thirds with the mixture of glycol and water, 1 to 2 drops of hydrochloric acid being added to the contents of every four tubes. In the case of propylene chloride, when it is heated with water, it first yields monochloropropylene and propyl-glycol, the latter being subsequently converted into propaldehyde, and the former into acetone. Thus:—

$$CH_3.CCl=CH_2 + H_2O = CH_3.CO.CH_3 + HCl.$$

Propylene bromide gives only monobromo-propylene and no propyl-glycol, so that the ultimate product is acetone. T. C.

Ethylvinyl Oxide. By J. WISLICENUS (*Liebig's Annalen*, cxcii, 106—128).—In order to prepare ethylvinyl ether, small pieces of sodium are from time to time dropped into a retort containing chloracetal, which is heated at 130—140° by means of an oil-bath, and the vapours which distil over are passed through a condenser, and collected in a receiver surrounded by ice. The ethylvinyl oxide and unaltered chloracetal, of which the distillate is composed, can easily be separated by fractional distillation. The residue in the retort consists of sodium chloride and ethylate, and of ethenyltriethylate. The last-mentioned substance owes its origin to a secondary reaction, viz., to the action of sodium ethylate on ethenyltrichloride, which is formed when chloracetal comes in contact with sodium ethylate at high temperatures. The following equation represents the change which occurs:—

$$\begin{gathered} bNaCl + bNaOC_2H_5 + (a-b)CH_2Cl.CH(OC_2H_5).OC_2H_5 = \\ (b + c)NaCl + (b-c)NaOC_2H_5 + \\ (a-b-c)CH_2Cl.CH(OC_2H_5).OC_2H_5 + \\ CH_2(OC_2H_5).CH(OC_2H_5).OC_2H_5. \end{gathered}$$

Ethylvinyl oxide, $CH_2=CH.OC_2H_5$, is a colourless mobile liquid, boiling at 35·5°, and burning with a luminous flame. Its sp. gr. is 0·7625 at 14·5° compared with water at 17·5°. Chlorine gas, diluted with twice its volume of carbonic anhydride, is completely absorbed by well-cooled ethylvinyl oxide, dichlorethyl oxide, $C_4H_8Cl_2O$ (b. p. 147°) being formed, $CH_2{=}CH.OC_2H_5 + Cl_2 = CH_2Cl.CHCl.OC_2H$: this was confirmed by its conversion into chloracetal by treatment with sodium ethylate. The corresponding dibromethyl oxide, $C_4H_8Br_2O$, is obtained by gradually adding a solution of bromine in carbon bisulphide to a mixture of carbon bisulphide and ethylvinyl oxide. The crude product cannot be purified by distillation, as it decomposes on boiling. Dibromethyl oxide decomposes slowly at the ordinary temperature, and is easily converted into bromacetal (b. p. 171°) by treatment with sodium ethylate.

The action of iodine on ethylvinyl oxide does not yield di-iodoethyl oxide, but appears to form an oxidised polymeride of ethylvinyl oxide.

Dilute sulphuric acid splits up ethylvinyl oxide sharply into aldehyde and ethyl alcohol. Water acts in a similar way, even at the ordinary temperature, but very slowly. W. C. W.

Derivatives of Milk Sugar. By H. FUDAKOWSKI (*Deut. Chem. Ges. Ber.*, xi, 1069—1076).—By the action of dilute sulphuric acid on milk-sugar, lactoglucose and galactose are formed (*Ber.*, ix, 42), the former yielding gluconic acid on oxidation, and the latter mucic acid. Air-dried *lactoglucose* melts at 70—71°, but when dried at 100° it melts at 132—135°. It resembles grape sugar in its reducing properties; 1 molecule of lactoglucose reducing 5 molecules of copper sulphate. *Galactose* crystallises in anhydrous prisms, which are frequently grouped together, forming granular nodules; 1 part of galactose is soluble in 167 parts of 85 per cent. alcohol at 20°. The melting point of the air-dried substance is 118—120°; that dried at 100° melts at 142—144°. It is a less energetic reducing agent than grape sugar, 1 molecule reducing only 4 molecules of copper sulphate. *Pentacetylgalactose*, $C_6H_7(C_2H_3O)_5O_6$, formed by the action of acetic anhydride on galactose, is a pale gum-like substance, soluble in alcohol, and precipitated from its alcoholic solution by water. It softens at 62°, and melts at 66—67°. The corresponding lactoglucose compound softens at 47° and melts at 51°. Galactose forms with baryta the compound $4(C_6H_{11}O_6)Ba_2.BaO$. By the action of 2 parts of nitric acid, sp. gr. 1·4, on milk sugar, 13·01 per cent. of mucic acid (dried at 100°) is obtained. Galactose under similar treatment yields 49·35 per cent. of mucic acid: hence the author concludes that 26·36 per cent. of milk sugar consists of galactose.

Both lactose and galactose form crystalline compounds with sodium chloride. Galactose is not completely precipitated by a dilute solution of lead acetate in presence of ammonia, but it is completely precipitated from an alcoholic solution by alcoholic potash. Its behaviour with ammoniacal silver nitrate, basic bismuth nitrate, indigo solution, and dilute solution of picric acid, is identical with that of glucose.

The sugar existing in small quantity in the muscles of the heart of a freshly-killed ox does not appear to yield mucic acid on oxidation. No mucic acid is formed by treating with nitric acid the sugar obtained by digesting linseed emulsion with artificial gastric juice (an extract of the mucous membrane of a pig's stomach in glycerin) containing 0·37 per cent. of free hydrochloric acid.

The sugars produced when arabic acid is subjected to similar treatment, yield oxalic but no mucic acid.

By digesting arabin in water containing 0·26 per cent. of hydrochloric acid, 2 per cent. of sugar is formed; but if pepsin is added to the mixture, the amount of sugar increases to 3·17 per cent. The action of the pancreas ferment on arabin is not analogous to that of pepsin. By oxidising a cold alkaline or hot neutral solution of dulcite with potassium permanganate, an optically inactive substance is formed, which is very soluble in alcohol, and resembles the glucoses in its reducing properites. It is easily decomposed by an alkaline solution of potassium permanganate. W. C. W.

Action of Potassium Hydrate on Quercite. By L. PRUNIER (*Compt. rend.*, lxxxvi, 1460—1462).—Quercite, when heated with solution of potash, is progressively attacked as the solution becomes more concentrated and the temperature higher, the action being marked at 200—250°. The products are quinone, pyrogallic acid, oxalic acid, and possibly malonic acid, $C_6H_4O_8$. R. R.

Starch. By MUSCULUS and GRUBER (*Compt. rend.*, lxxxvi, 1459—1460).—Under the influence of dilute boiling sulphuric acid or of diastase, the following different substances are produced from starch:—

1. *Soluble Starch.*—This substance is insoluble in water at 50—60°. It is coloured wine-red by iodine when it is in aqueous solution, and blue when it is in the solid state. Dried in the air with excess of iodine, it assumes violet, yellow, or brown tints. Its rotatory power is $[\alpha] = + 218°$, and its reducing power is 6.

2. *Erythrodextrin*, which constitutes half of the dextrin of commerce, always strikes a red colour with iodine, whether it be solid or in solution. It is never insoluble in water. The smallest quantity of diastase easily attacks soluble starch as erythrodextrin.

3. *Achroodextrin* α, is not coloured by iodine. Rotatory power $[\alpha] = + 210°$; reducing power, 12. Partially convertible into sugar by diastase, but less easily than soluble starch or erythrodextrin.

4. *Achroodextrin* β, not attacked by diastase at least during the first 24 hours. Rotatory power $[\alpha] = + 190°$; reducing power, 12.

5. *Achroodextrin* γ; not attacked by disastase at all; changed into glucose by boiling with dilute sulphuric acid for several hours. Rotatory power $[\alpha] = + 150$; reducing power, 28.

6. *Maltose* $(C_{12}H_{22}O_{11} + H_2O)$; attacked with difficulty by fermentable diastase. Rotatory power $[\alpha] = + 150°$; reducing power, 66.

7. *Glucose* $(C_6H_{12}O_6 + H_2O)$; fermentable. Rotatory power $[\alpha] = + 56°$; reducing power, 100.

The authors regard starch as a polysaccharide of the formula $n(C_{12}H_{20}O_{10})$, in which the exact value of n, which apparently is not less than 5 or 6, remains to be determined. Under the influence of diastatic ferments and of dilute acids, this hydrate of carbon by successive stages takes up water and breaks up into maltose and a new dextrin of successively smaller molecular weight; n becomes less for each stage, until the production of the achroodextrin γ, which is probably transformed into maltose by simple hydration, and the maltose in its turn takes up water and splits up, thus:—

$$C_{12}H_{22}O_{11} + H_2O = 2(C_6H_{12}O_6).$$

R. R.

Direct Conversion of Isobutyl Iodide into Trimethylcarbinylamine. By B. BRAUNER (*Liebig's Annalen*, cxcii, 65—80). —Several years ago Linnemann pointed out (*Annalen*, clxii, 19) that trimethylcarbinylamine is produced by the action of isobutyl iodide on silver cyanate. Subsequently, however, Hofmann, on repeating the experiment, obtained chiefly isobutylamine, and not trimethylcarbinylamine. In order to clear up these conflicting results, the author has, under Linnemann's directions, re-investigated the above reaction.

The isobutyl iodide employed was purified with very great care. It boiled at 120° (corr.) under a pressure of 760 mm.; its specific gravity at 0° = 1·6401 and at 20° = 1·6050; its coefficient of expansion for 1° between 0 and 20° = 0·0110. One hundred grams of the iodide were treated for 4 hours at 70—80° with 84 grams of dry silver cyanate in a flask, provided with a reversed condenser. Each 46 grams of the dry mass thus obtained was heated with 30 grams of finely-powdered potash, and the resulting ammoniacal vapours passed into hydrochloric acid: a small quantity of gas was simultaneously evolved, whilst a little oily substance collected in the acid. After separation of the oil, the hydrochloric acid solution was found to consist *chiefly* of the hydrochlorides of trimethylcarbinylamine and ammonia, besides some isobutylamine. The free trimethylcarbinylamine agreed in all respects with that previously obtained by Linnemann. It boiled at 46·°4 (corr.); its specific gravity at 0° = 0·7155, and at 15° = 0·7004; its coefficient of expansion from 0° to 15° = 0·00142; its vapour density likewise agreed with the calculated value.

The salts of the base are quite distinct from those of isobutylamine.

Trimethylcarbinylamine hydrochloride had the same properties as those previously described by Linnemann. It melts at 270—280°, whilst the corresponding salt of isobutylamine melts at 160°.

The double platinum salt is a bright orange-yellow powder, crystallising from water in sword-shaped prisms. It is rather difficultly soluble in cold alcohol, but easily soluble in hot, from which solution it crystallises only after long standing in beautiful monoclinic prisms of the combination, 0P, ∞Pm, Pm, +P. The corresponding salt of isobutylamine crystallises in microscopic rhombic plates. The sulphates, nitrates, and oxalates of the two bases were also made and compared. The author explains the formation of trimethylcarbinylamine by the above reaction as follows:—The isobutyl iodide acts first on the silver cyanate to form silver iodide, cyanic acid, and isobutylene. The isobutylene goes off as a gas, whilst the cyanic acid unites with another molecule of silver cyanate to form an "acid dicyanate of silver," which in turn acts on another molecule of isobutyl iodide, with production of silver iodide and an acid dicyanate of trimethylcarbinol, and this latter when heated with potash gives ammonia and trimethylcarbinylamine. Thus:—

$$\text{I. } 2Ag(NCO) + (CH_3)_2.CH.CH_2I = AgI + (CH_3)_2.C{=}CH_2 + AgH(NCO)_2.$$

$$\text{II. } AgH(NCO)_2 + (CH_3)_2.CH.CH_2I = AgI + C(CH_3)_3.H(NCO_2).$$

$$\text{III. } C(CH_3)_3.H(NCO)_2 + 4KHO = 2K_2CO_3 + NH_3 + C.(CH_3)_3.NH_2.$$

These equations are confirmed by a number of stoïchiometrical determinations. T. C.

Trimethylglyceramine. By HANRIOT (*Compt. rend.*, lxxxvi, 1335—1336).—This body is obtained by heating monochlorhydrin with commercial trimethylamine, until the odour of the latter is no longer perceptible. To this liquid, a concentrated solution of platinum chloride is added, and on standing, ammonium-platinum chloride separates out; the filtrate from this, when evaporated, yields a crystalline mass, whilst the mother-liquor contains an uncrystallisable body, which is precipitated by alcohol, and appears to be the chloroplatinate of monomethylglyceramine. The crystalline mass, purified by pressure and crystallisation, yields orange-coloured tables, apparently belonging to the orthorhombic system. These crystals, the platinum salt of trimethylglyceramine, $\{(C_3H_7O_2)(CH_3)_3NCl\}_2PtCl_4$, are soluble in cold and hot water; the aqueous solution is not decomposed on boiling. They are insoluble in alcohol, and lose hydrochloric acid on exposure in a vacuum.

The chloroplatinate, heated with sulphuretted hydrogen, yields the hydrochloride of the base as a colourless syrupy liquid, which yields the corresponding hydrate when treated with silver oxide. P. P. B.

Ethylic Guanidine-Carbonate. By M. NENCKI (*J. pr. Chem.*, [2], xvii, 237—239).—When guanidine is brought into contact with chlorocarbonic ether, the temperature rises, and ethylic guanidine-dicarbonate and guanidine chloride are formed. Ethylic guanidine-dicarbonate, heated in a closed tube at 100° with alcoholic ammonia, yields a base to which the author formerly (*Ber.*, 1874, p. 1589) assigned the formula $C_8N_6H_{18}O_4$, and the name guanoline. This body, from an analysis of the nitrate, is now found not to have the double formula, but the simple one, $C_4N_3H_9O_2$. This is also the empirical formula of guanidine-monocarbonic ether, $HN{=}C(NH_2).NH.COOC_2H_5$, and the author has no doubt that guanoline is this ether. These results compared with those of Bässler (*J. pr. Chem.* [2], xvi, 125) on the behaviour of chlorocarbonic ether to cyanamide show that a remarkable agreement exists between guanidine and cyanamide in their behaviour to reagents; and this would indicate a similarity in the molecular structure of the two bodies. G. T. A.

Maxwell Simpson's Syntheses of Acrolein from Diiodacetone. By O. VÖLKER (*Liebig's Annalen*, cxcii, 89—105).—*Symmetrical diiodacetone*, $CH_2I.CO.CH_2I$. — A mixture of iodine trichloride and acetone, in the proportion of 1 mol. of the former to 2 of the latter, is heated over a lamp with 20 volumes of water until the temperature reaches 66°; it is then quickly cooled and left at rest for 12 hours, when a heavy oil separates out, which possesses a very penetrating odour, and attacks the eyes and mucous membrane powerfully. After decanting the supernatant liquid, the oil is exposed to the air in shallow vessels for several weeks, when it in great part volatilises, but deposits crystals of the diiodacetone, which are purified by recrystallisation from alcohol. The crude oil contains, in addition to diiodacetone, iodine monochloride, moniodo- and monochloracetone. Its formation probably takes place according to the following equation:—

$$3ICl_3 + 4C_3H_6O = ICl + 5HCl + C_3H_4I_2O + 3C_3H_5ClO.$$

Pure diiodacetone crystallises in white needles (m. p. 62°) which are soluble in benzene, ether, and acetone, and sparingly soluble in cold alcohol, chloroform, and carbon bisulphide. The skin is burnt when brought in contact with this substance, and the eyes and mucous membrane are attacked by its vapour. Diiodacetone begins to decompose at 120°, giving off vapours of iodine and hydriodic acid. The constitution of this substance is shown to be $CH_2I.CO.CH_2I$, since it can be formed by the action of potassium iodide on symmetrical dichloracetone, $CH_2Cl.CO.CH_2Cl$. Moreover, when acted on by silver chloride, it yields symmetrical dichloracetone. The density of the vapour of dichloracetone was found to be 63·5; this shows that Barbaglia's hypothesis (*Ber.*, vii, 469) that this body is bimolecular is incorrect.

Maxwell Simpson states in *The Laboratory*, that acrolein is formed by treating diiodacetone with silver cyanide; the author, however, finds that no trace of this body is produced, either by the action of silver cyanide or oxide, or of mercuric oxide, on diiodacetone. With mercurous iodide in presence of water it yielded acetone. *Dibromacetone*, $C_3H_4OBr_2$, prepared by the action of silver bromide on diiodacetone, or by boiling dichloracetone with potassium bromide, melts at 24°, and is readily soluble in ether and carbon bisulphide, and is therefore quite distinct from acrolein bromide, $C_3H_4Br_2O$, which melts at 66°, and is insoluble in carbon bisulphide. W. C. W.

An Improved Mode of Preparing Substituted Acetoacetic Ethers. By M. CONRAD and L. LIMPACH (*Liebig's Annalen*, cxcii, 153—160).—Instead of allowing the sodium to act on a mixture of benzene and acetoacetic ether, the sodium is dissolved in absolute alcohol, and the ethylic acetoacetate added to the solution: for example, in order to prepare ethylic ethyl-acetoacetate, 32·5 grams of ethylic acetoacetate are added to a solution of 5·7 grams of sodium in 70 grams of absolute alcohol, and 40 grams of ethyl iodide are gradually brought into the mixture. After heating in a flask provided with an upright condenser until the liquid ceases to have an alkaline reaction, most of the alcohol is distilled off, and the oily layer in the flask is dried over potassium carbonate and distilled: 32·5 grams of ethylic ethyl-acetoacetate, boiling at 190—196°, were obtained. The ethylic ethyl-acetoacetate may be easily converted into ethylic diethylacetoacetate in a similar manner. To prepare ethylic acetosuccinate, ethyl monochloracetate is added to the mixture of sodium ethylate and ethylic acetoacetate. An alcoholic solution of potash may be substituted for the sodium ethylate, but the results obtained are not so satisfactory. The advantages of this process are that it yields very pure products; as bye-products are not formed; the substituted ethers are obtained in a state of purity, and need not, therefore, be extracted from their alcoholic solution in order to study the products of their decomposition by alcoholic potash.

Ethylic acetomalonate cannot be prepared by this method.

W. C. W.

Ethylic α-β-Dimethylacetosuccinate and Symmetrical Dimethylsuccinic Acid. By F. HARDTMUTH (*Liebig's Annalen*, cxcii, 142—146).—*Ethylic α-β-dimethylacetosuccinate*,

$$CH_3.CO.C(CH_3)(COOC_2H_5).CH(CH_3).COOC_2H_5,$$

prepared by dissolving sodium in α-ethylic β-methylacetosuccinate diluted with an equal volume of benzene, and heating the mixture with methyl iodide for two hours in a flask connected with an upright condenser, is an oily liquid boiling at 270—272°, with a sp. gr. of 1·057 at 27°. This ether is decomposed by boiling with alcoholic potash, forming symmetrical dimethylsuccinic acid, acetic, and carbonic acids, and a ketonic acid, which boils between 210° and 220°, and is probably acetopentylic acid, $C_7H_{12}O_3$.

Symmetrical dimethylsuccinic acid,

$$CH_3.CH(COOH).CH(CH_3).COOH,$$

is a crystalline mass melting at 165—167°. W. C. W.

Ethylic α-Ethylacetosuccinate and α-Ethylsuccinic Acid. By C. HUGGENBERG (*Liebig's Annalen*, cxcii, 146—152).—Ethyl iodide readily acts on ethylic sodacetosuccinate mixed with benzene, forming *ethylic α-ethylacetosuccinate*, which is a colourless liquid boiling at 263—265°. Unlike the corresponding β-ether, sodium has no action on this substance even at 100°.

Ethylic α-ethylacetosuccinate is decomposed on boiling with alcoholic potash, splitting up into β-acetopentylic,

$$CH_3.CO.CH(C_2H_5).CH_2.COOH,$$

α-ethylsuccinic, and acetic acids.

α-Ethylsuccinic acid, $C_2H_5.CH(COOH).CH_2.COOH$, crystallises in white non-deliquescent prisms (m. p. 98°) which are very soluble in water, alcohol, and ether. The potassium, sodium, and barium salts of this acid do not crystallise.

Calcium ethylsuccinate, $C_6H_8CaO_4 + 2H_2O$, forms colourless prisms: the silver salt is precipitated as a white powder on adding barium ethylsuccinate to silver nitrate. The ethylic salt of this acid, $C_{10}H_{18}O_4$, boils at 222—225°. W. C. W.

Action of Potassium Iodide on β-Dibromopropionic Acid. By V. v. ZOTTA (*Liebig's Annalen*, cxcii, 102—105).—On boiling β-dibromopropionic acid with an aqueous solution of potassium iodide, acrylic acid and free iodine are formed, but no iodine addition-product of acrylic acid is obtained. W. C. W.

Compounds of Pyroracemic Acid with the Sulphites of the Alkalis and Alkaline Earths. By C. CLEWING (*J. pr. Chem.* [2], xvii, 241—266).—The author's object is to show that pyroracemic acid is the lowest of the ketonic acids, and may be written as $CH_3.CO.COOH$.

This view is supported by the fact that pyroracemic acid splits up very easily into formic and acetic acids, a point in which it resembles acetone. It also forms a number of salts with sulphites of the alkalis and alkaline earths such as $C_3H_4O_3.HSO_3Na$; $C_3H_4O_3.HSO_3K$; $C_6H_6O_6Ca + 4(C_3H_3O_3.Ca.HSO_3).24H_2O$; $2(C_3H_3O_3.Sr.SO_3H).5H_2O$; $C_3H_3O_3.Ba.HSO_3$, &c. These salts are all tolerably stable, and resemble each other in character. Pyroracemic acid also forms crystalline compounds with neutral sodium and potassium sulphites, $C_3H_3KO_3.HSO_3K + H_2O$, $C_3H_3NaO_3.HSO_3Na + H_2O$ and $2[C_3H_3NaO_3.HSO_3Na] + H_2O$; but it is not homologous with glyoxylic acid, since, although it yields lactic acid by the action of nascent hydrogen, no malonic acid is formed on oxidation, but, among other products, oxalic acid. The following papers are referred to: *Annalen*, cxxvi, 145 and 229; cxxvii, 336; clxxii, 262; cxliv, 352; clii, 268; *Deut. Chem. Ges. Ber.*, 1874, 596. G. T. A.

Easy Method of Preparing Trichlorethylidenelactic Ether. By M. NENCKI (*J. pr. Chem.* [2], xvii, 239—240).—This is done by heating chloral hydrate with the equivalent quantity of syrupy lactic acid on a water-bath, and adding about as much concentrated sulphuric acid by weight as that of the chloral employed. On addition of water, the ether separates as a heavy oil. It is freed from sulphuric acid by washing and drying over calcium chloride. G. T. A.

Synthesis of Pyrotartaric Acid by means of Ethylic α-Methylacetosuccinate. By G. KRESSNER (*Liebig's Annalen*, cxcii, 135—141).—*Ethylic α-methylacetosuccinate*, formed by the action of methyl iodide on a solution of ethylic sodacetosuccinate in benzene, is an oily liquid boiling at 263°, and having a sp. gr. of 1·067. On boiling with alcoholic potash, it splits up, yielding the potassium salts of acetic and methylsuccinic acids.

The methylsuccinic acid, $C_5H_8O_4$, prepared from the pure silver salts, forms white crystals (m. p. 111·5°) soluble in water and in ether, and is identical with pyrotartaric acid. W. C. W.

Synthesis of Glutaric and α-Methylglutaric Acids. By J. WISLICENUS and L. LIMPACH (*Liebig's Annalen*, cxcii, 128—135).—Ethylacetoglutarate is formed by the action of 1 mol. of ethyl β-iodopropionate on a solution of 1 atom of sodium in 1 mol. of ethylacetoacetate diluted with an equal volume of benzene. The reaction begins at the ordinary temperature, and is completed by heating at 100° in a flask provided with an upright condenser. The mixture is shaken up with water, and the oily liquid which separates is dried and distilled. Ethylic acetoglutarate, $C_{11}H_{18}O_5$, boils at 271—272°, and has a sp. gr. of 1·0505 at 14° compared with water at 17·5°.

By saponifying this substance with alcoholic potash, decomposing the potassium salt thus obtained with dilute sulphuric acid, and extracting with ether, a mixture of acetic and glutaric acids is obtained.

The acetic acid distils over when this mixture is heated to 130° in an oil-bath, leaving the glutaric acid, $C_5H_8O_4$, in the form of a thick syrup, which solidifies on cooling to a crystalline mass, identical in every respect with the glutaric acid obtained by the action of hydriodic acid on trimethene cyanide.

Ethylic α-methylglutarate, prepared by the action of ethylic methylsodacetoacetate on β-ethylic iodopropionate, boils at 280—281°, and has a sp. gr. of 1·043 at 20° compared with water at 17·5°. Its formation may be represented thus:—

$$CH_3.CO.CNa(CH_3).CO.OC_2H_5 + ICH_2.CH_2.COOC_2H_5 = NaI + CH_3.CO.C(CH_3)(CH_2.CH_2.COOC_2H_5).COOC_2H_5.$$

By saponification with alcoholic potash the potassium salt of *α-methylglutaric acid*, $CH_3.CH(COOH).CH_2.CH_2.COOH$, is obtained. The acid is a crystalline body (m. p. 76°) very soluble in water, alcohol, and ether. The zinc salt is an amorphous mass, soluble in water and alcohol; the silver salt, $C_6H_8Ag_2O_4$, is an amorphous white powder.

W. C. W.

Carbocomenic Acid and the Ether of Carbogallic Acid.

By E. DRECHSEL and H. MÖLLER (*J. pr. Chem.* [2], xvii, 163—164).—When a solution of ethyl-comenic acid in absolute alcohol is mixed with a similar solution of one molecule of sodium alcoholate, a yellow, apparently amorphous precipitate is thrown down, which on addition of a molecule of chlorocarbonic ether and digestion on the water-bath, becomes white. This is filtered off, the solution evaporated, and the residue crystallised from hot water.

The crystals consist of fine white silky needles and plates which dissolve with difficulty in cold water, but are readily taken up by alcohol and ether, and melt at 87° (uncorrected). This compound is isomeric with diethylmeconic acid (m. p. 110°), and on saponification, which takes place with facility, the corresponding acid itself splits up into carbonic and comenic acids. If the latter is dibasic and sodium ethylcomenate is $C_4H_2O(COOC_2H_5)(COONa)$, the new compound is $C_4H_2O(COOC_2H_5)(COO.COOC_2H_5)$. Apparently this ether is the first representative of a new series of ethereal salts, which may be prepared in a similar manner. Carbogallic ether, which has been obtained, crystallises in small white needles, is easily soluble in alcohol, less readily in ether: its melting point is 116·5° (uncorrected).

G. T. A.

Artificial Malic Acid from Fumaric Acid.

By F. LLOYD (*Liebig's Annalen*, cxcii, 80—89).—By the following process 60 parts of malic acid can be obtained from 100 parts of fumaric acid. A mixture of 1 part of fumaric acid, 4 of caustic soda, and 40 of water is heated at 100° in a closed metallic vessel for 100 hours. When the reaction is complete, the quantity of sodium carbonate and hydrate in the product is determined by titration, and sufficient sulphuric acid is added to set free almost all the malic acid. After evaporating the mixture to dryness, and treating the residue with ether to dissolve out the fumaric and malic acids, the crystalline mass, which remains on distilling off the ether, is broken up and exposed to a moist atmosphere; the malic acid then deliquesces, and the fumaric acid remains undissolved. Artificial malic acid, purified by recrystallisation, forms a hard white crust composed of microscopic crystals. It is deliquescent, but does not absorb water so rapidly as natural malic acid; its solution is optically inactive. The acid melts at 132—136°, begins to decompose at 178°, and at 200° splits up into water and fumaric acid, but not a trace of malic acid is formed. The following salts were prepared:

$C_4H_4CaO_5$ and $C_4H_4CaO_5 + H_2O$ precipitated by boiling a mixture of the malic acid and lime-water, are less soluble in cold than in hot water. The acid calcium malate, $C_4H_4'CaO_5.C_4H_6O_5 + H_2O$, is formed by dissolving the neutral salt in aqueous malic acid, but it does not separate out, on the addition of nitric acid, to neutral calcium malate. Lead and silver malates are sparingly soluble amorphous powders; sodium and copper malates do not crystallise; the zinc and barium salts can be obtained in the crystalline form, but the acid ammonium malate is the only salt which really crystallises well.

This artificial malic acid differs in its properties from natural optically active malic acid, also from Kekulé's optically inactive acid from monobromosuccinic acid (*Annalen*, cxvii, 120), but it resembles in certain respects the acid which Pasteur obtained from optically inactive aspartic acid (*Annalen*, lxxxii, 324). The author points out that the isomerism of these acids cannot be expressed by means of the ordinary structural formulæ, although it can be clearly explained by van t'Hoff's symbols. W. C. W.

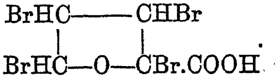
Ammoniacal Citrates. By E. LANDRIN (*Compt. rend.*, lxxxvi, 1336—1338).—The author has investigated the cause of the solubility of certain oxides and metallic citrates in ammonium citrate. Calcium oxide or precipitated calcium carbonate both decompose ammonium citrate, forming tricalcic citrate, which is soluble in ammonium citrate. Strontia and baryta behave in exactly the same manner. In the case of magnesia, however, a double salt is formed, soluble in water, and slightly soluble in alcohol. By evaporating its aqueous solution over sulphuric acid, crystals having the composition $(C_6H_5O_7)_2(NH_4)_4Mg + 2H_2O$ are obtained.

Gelatinous alumina boiled with ammonium citrate forms a double salt, and ferric oxide yields a similar compound crystallising in yellow crystals containing 6 mols. of water; these become brown on exposure to the air.

Hydrates of cobalt and nickel decompose citrate of ammonia, yielding double salts, having the composition $(C_6H_5O_7)_2(NH)_4M'' + 4H_2O$.

Manganese carbonate yields an anhydrous salt $(C_6H_5O_7)_2(NH_4)_4Mn$, whilst copper carbonate gives one of the composition $(C_6H_5O_7)_2(NH_4)_4Cu + H_2O$. P. P. B.

Action of Bromine on Pyromucic Acid. By P. TÖNNIES (*Deut. Chem. Ges. Ber.*, xi, 1085—1088).—*Tetrabromide of ethyl pyromucate*, $C_5H_3Br_4O_3.C_2H_5$, is prepared by exposing ethyl pyromucate to an atmosphere of dry bromine vapour for 12 hours at the ordinary temperature; the product is treated with a small quantity of liquid bromine; and the excess of bromine is removed by means of sulphurous acid. This body is deposited from its solution in chloroform in colourless crystals which melt at 46—48°, and decompose at a higher temperature. It is converted into ethyl pyromucate by the action of sodium amalgam.

Pyromucic acid tetrabromide, formed by the action of dry bromine vapour on pyromucic acid, is a white crystalline body, easily soluble in alcohol and ether, sparingly so in chloroform and petroleum ether. It contains four atoms of bromine in addition to the elements of pyromucic acid, and has the formula  It is insoluble in cold water, and is decomposed by hot water, with evolution of carbonic and hydrobromic acids. By the action of reducing agents pyromucic acid is formed, but on oxidation with chromic acid dibromo-succinic acid is obtained. The tetrabromide melts at 159—160° with decomposition, bromine and hydrobromic acid escape, and needle-shaped crystals of a new acid (m.p. 180°) sublime.

Dibromo-pyromucic acid, $C_5H_2Br_2O_3$, is prepared by the action of solution of potash on the tetrabromide. It crystallises in colourless scales, which melt at 184—186°, and at a higher temperature sublime without decomposition. W. C. W.

Synthesis of Cyanacetyl-ureas and Murexoïne. By E. MULDER (*Bull. Soc. Chim.* [2], xxix, 531—535).—In order to prepare acetylmalonic anhydride the author endeavoured to obtain acid silver malonate by the action of equivalent quantities of silver nitrate and acid sodium malonate on each other. Neutral silver malonate, however, was always obtained, which, when treated with acetyl chloride, did not give the required result.

Neutral sodium malonate was obtained by treating the acid sodium salt with sodium bicarbonate in a desiccator over lime; on adding alcohol to the aqueous solution of the product, the neutral salt separated out in crystals, $CH_2(COONa)_2 + H_2O$. It loses water at 130°. It is slowly attacked by acetyl chloride, yielding a red mass, but no malonic anhydride. By the action of PCl_5 on malonic acid malonyl chloride, $COCl.CH_2.COCl$, is formed, but cannot be separated from the phosphorus oxychloride. If potassium ethyl malonate be distilled with $POCl_3$ a mixture of ethyl malonate and potassium malonate is obtained—

$$2C_2H_5O.CO.CH_2.COOK = C_2H_5O.CO.CH_2.COOC_2H_5 + (COOK)_2.$$

Cyanacetic acid is not attacked by acetyl chloride, but on treating it with phosphorus pentachloride, cyanacetyl chloride is formed, and on addition of carbon bisulphide, separates out as a colourless liquid. This slowly undergoes polymerisation, being converted into a dark-coloured solid mass. When heated with urea, it yields *cyanacetylurea*, $CN.CH_2.CO.NH.CO.NH_2$. This compound is soluble in alcohol, from which it crystallises in needles, whilst the aqueous solution yields plates. It melts between 200 and 210°, decomposing at the same [illegible] When saponified, the molecule is always broken up, and urea [illegible]

Cyanacetyldimethylurea, $CN.CH_2.CO.N(CH_3).CO.NH.(CH_3)$, is obtained by the action of cyanacetyl chloride on dimethylurea; it is very stable, and can be heated to 260° without decomposing. When treated with nitric acid, cyanacetyldimethylurea yields a reddish-purple compound, which loses its colour when the aqueous solution is heated, or when treated with potash. It appears to be Rochleder's murexoïne (a derivative of theine) or an analogous compound. L. T. O'S.

Chlorodinitrocymene, Bromodinitrocymene, and so-called Solid Nitrocymene. By E. v. GERICHTEN (*Deut. Chem. Ges. Ber.*, xi, 1091—1093).—An oily liquid (probably a chloronitrocymene) is formed on cautiously adding chlorocymene (m. p. 214°) to nitric acid, sp. gr. 1·5, and pouring the crude product into water; but on treating the chlorocymene with a mixture of equal parts of fuming nitric and sulphuric acids, a mixture of an oily compound with crystals of dinitrochlorocymene, $C_{10}H_{11}(NO_2)_2Cl$, is obtained. This body crystallises in yellowish-white monoclinic prisms (m.p. 108—109°), which dissolve readily in hot, but sparingly in cold alcohol. It is isomeric with Ladenburg's dinitrochlorocymene (m.p. 100—101°) from dinitrothymol, and is $CH_3 : Cl = 1 : 2$.

Dinitrobromocymene prepared from bromocymene (m.p. 228—229°) resembles the dinitrochlorocymene in its mode of preparation and in its properties.

The author has previously pointed out (*Ber.*, x, 1251) that, by the action of cold concentrated sulphuric acid on the so-called "solid nitrocymene" (m.p. 124°) he obtained paratoluic acid (m.p. 177°), and not nitro-cymenesulphonic acid, as stated by Fittica. He now finds that this so-called nitrocymene dissolves in boiling potash, and on the addition of dilute sulphuric acid to the solution, paratoluic acid is precipitated. The fact that this compound contains only 4·5 per cent. of hydrogen instead of 7·2 shows that it is not a nitrocymene.

W. C. W.

Compounds of Cobalt Chloride with Aniline. By E. LIPPMANN and VORTMANN (*Deut. Chem. Ges. Ber.*, xi, 1069).—When an alcoholic solution of cobalt chloride is added to aniline, a pale red precipitate separates out, which has the composition, $2C_6H_7N + CoCl_2 + 2C_2H_6O$. On heating this substance at 100° its colour changes to blue, the compound $2C_6H_7N + CoCl_2$ being formed.

This blue salt can also be obtained in glistening blue needles by heating together anhydrous cobalt chloride and aniline, and recrystallising the crude product from absolute alcohol. W. C. W.

Preparation of Dimethylaniline from Trimethylphenylammonium Iodide. By N. F. MERRILL (*J. pr. Chem.* [2], xvii, 286—287).—The perfectly dry iodide is distilled in a stream of dry hydrochloric acid gas, when the following decomposition takes place—

$$C_6H_5(CH_3)_3NI + HCl = C_6H_5(CH_3)_2N.HCl + CH_3I.$$

If two receivers are used it is possible with practice to collect the two bodies separately, the first receiver being kept moderately cool, the second well cooled. G. T. A.

Amidines and Thiamidines of Monobasic Organic Acids. By A. BERNTHSEN (*Liebig's Annalen*, cxcii, 1—60).—In two earlier communications (*Annalen*, clxxxiv, 290—321, this Journal, 1877, i, 616) the author has described the thiamide of phenylacetic acid, and the amidines of monobasic organic acids. It was there shown that amidines of the form—

$$R'(NH_2)C\equiv NH, \text{ or } R'(NH_2)C\equiv NR', \text{ or } R(NHR')C\equiv NH,$$

can be obtained by the action of amine bases, both on thiamides and on nitrils of monobasic acids. The author has not been able to obtain doubly substituted amidines $R(NHR'')C\equiv NR'$, with a constitution similar to those described eleven years ago by Hofmann (*Zeit. f. Chem.*, 1866, 161), by the direct addition of the nitrils and secondary amine bases, for by this method amidines of the form $R(NR'R'')C\equiv NH$, are produced isomeric with those obtained by Hofmann.

Benzenylisodiphenylamidine, $C_6H_5[N(C_6H_5)_2]C\equiv NH$ (*Deut. Chem. Ges. Ber.*, x, 1235). This substance, formed by the action of benzonitril on diphenylamine hydrochloride at 180°, crystallises in rhombic prisms or tables (m.p. 112°), which are extremely soluble in benzene and alcohol, and moderately in warm ether. It is a powerful base, absorbing carbonic acid from the air. With concentrated sulphuric and a drop of nitric acid it shows no diphenylamine reaction at the ordinary temperature, but on boiling gives a violet-blue coloration. It differs, therefore, in all respects from the isomeric base obtained by Hofman (m.p. 144°), which is neutral, and only moderately soluble in alcohol and benzene.

The hydrochloride crystallises in prisms or needles, melting with decomposition at 223°. It is very easily soluble in water and alcohol, but scarcely soluble in ether. The *platinum salt* is a yellow powder.

The nitrate is rather difficultly soluble in water and alcohol, and crystallises in large transparent prisms (m.p. about 115°).

The thiocyanate, obtained as a bye-product, by the action of carbon bisulphide on benzenylisodiphenylamidine, crystallises in colourless prisms (m.p. 203°), which are difficultly soluble in cold water, but somewhat more soluble in hot benzene.

The *acid* and *neutral oxalates* are neither of them characteristic bodies.

On heating benzenylisodiphenylamidine in a flask provided with a reversed condenser, it splits up directly into benzonitril and diphenylamine.

Benzodiphenylamide or *diphenylbenzamide*, $C_6H_5.CO.N(C_6H_5)_2$, is obtained by heating benzenylisodiphenylamidine with water and a little hydrochloric acid at 180° for some hours. It crystallises in colourless rhombic needles (m.p. 176°), which on heating with concentrated sulphuric acid and alcohol, yield ethyl benzoate and diphenylamine. This substance, already prepared by Hofmann (*Annalen*, cxxii, 160), can also be obtained from benzoic chloride and diphenylamine. It is but little soluble in ether, cold alcohol, or cold water, but more easily in hot alcohol. Its formation from benzenylisodiphenylamidine confirms the above constitution for the latter body.

Benzenylisodiphenyl-methylamidine, $C_6H_5[N(C_6H_5)_2]C{=}N(CH_3)$. The iodide of this body is obtained by the action of methyliodide on benzenylisodiphenylamidine. The free base forms a colourless syrup. The hydrochloride, iodide, and nitrate are amorphous substances. The platinum salt is a bright yellow precipitate, which on addition of alcohol changes to a viscous mass.

Benzenylisodiphenylnitrosamidine, $C_6H_5[N(C_6H_5)_2]C{=}N{-}N{=}O$. The author has attempted to obtain this body by the action of ethyl nitrite on the free base in the cold. By this method he obtained a substance consisting of yellowish-white crystals, which on fusing with potassic hydrate showed Liebermann's phenolsulphonic acid reaction, so that it probably consisted of the desired product. It does not dissolve in dilute acids, but dissolves in alcohol and ether. It melts at 168°. The author has, however, not yet completed the investigation of this body.

Base $C_{19}H_{13}N$. As already described (*Ber.*, x, 1237), benzonitril, when heated with diphenylamine hydrochloride at 230—250°, gives the base $C_{19}H_{13}N$ instead of the amidine $C_{19}H_{16}N_2$. This substance has a neutral reaction; it is easily soluble in benzene, moderately soluble in ether, and but little soluble in hot or cold alcohol. It crystallises from benzene in large yellowish prisms, which quickly disintegrate in contact with the air. They contain 1 mol. of "benzene of crystallisation," thus—$C_{19}H_{13}N + C_6H_6$. Specimens free from benzene melt at 183°. With concentrated nitric acid the base gives a nitro-product, but is not acted on by acetyl chloride or chromic acid, nor by distillation over soda-lime. The *hydrochloride* forms garnet-coloured prismatic needles, which are insoluble in cold water, and melt above 220°. The composition of the *platinum salt* shows that the base is mono-acid. The *nitrate* is decomposed by pure water, but may be crystallised from water containing a little free nitric acid. The author has not been able as yet to make out the constitution of this base.

Ethenylisodiphenylamidine, $CH_3[N(C_6H_5)_2]C{=}NH$. This is obtained by heating acetonitril with diphenylamine hydrochloride at 140—150°. It crystallises with difficulty in monoclinic prisms (m.p. 63°), is strongly basic, and very easily soluble in cold alcohol, whilst the isomeric ethenyldiphenylamidine melts at 132°, is neutral, and only moderately soluble in cold alcohol. The *hydrochloride* is very easily soluble in water. The *platinum salt* is a deep yellow non-crystalline powder. The *sulphate* and *nitrate* are very easily soluble resinous masses; the thiocyanate is somewhat less soluble, and crystallises well.

By heating acetonitril with diphenylamine hydrochloride at 200° ammonia is evolved, and *the base* $C_{14}H_{11}N$ is obtained.

The author has previously shown (*Ber.*, x, 1238) that substituted thiamides are produced by the action of sulphuretted hydrogen on substituted amidines. Thus, when benzenylmonophenylamidine is exposed at 120—130° to the action of a slow current of the gas, benzothiamide, $C_6H_5.CS.NH_2$ (m.p. 116°), and benzothianilide, $C_6H_5.CS.NHC_6H_5$ (m.p. 98°), are formed, the latter of which is identical with that obtained by Leo (*Ber.*, ix, 1216) by the action of sulphuretted hydrogen on $C_6H_5.CCl{=}NC_6H_5$. These facts show that the reaction may take place simultaneously in two different directions, thus:—

$$\text{I. } C_6H_5(NH.C_6H_5)C{=}NH + H_2S = C_6H_5.CS.NH(C_6H_5) + NH_3.$$
$$\text{II. } C_6H_5(NH.C_6H_5)C{=}NH + H_2S = C_6H_5.CS.NH_2 + NH_2(C_6H_5).$$

a-Benzenyldiphenylamidine treated in a similar manner gives benzothianilide and aniline, thus:

$$C_6H_5(NH.C_6H_5)C{=}N(C_6H_5) + H_2S = C_6H_5.CS.NH(C_6H_5) + NH_2.C_6H_5,$$

whilst benzenylisodiphenylamidine (m.p. 112°) by the same reaction yields benzothiamide, diphenylamine, ammonia, and a new thiamide, viz., benzodiphenylthiamide, thus:—

$$\text{I. } C_6H_5[N(C_6H_5)_2]C{=}NH + H_2S = C_6H_5.CS.NH_2 + NH(C_6H_5)_2.$$
$$\text{II. } C_6H_5[N(C_6H_5)_2]C{=}NH + H_2S = C_6H_5.CS.N(C_6H_5)_2 + NH_3.$$

Benzodiphenylthiamide is insoluble in cold water, and only difficultly soluble in cold alcohol. It crystallises from benzene in dark-yellow crystals (m.p. 150°).

Formothianilide, $H.CS.NH(C_6H_5)$, is obtained by the action of sulphuretted hydrogen on methenyldiphenylamidine. It crystallises from dilute alcohol in brilliant yellow plates, melting at 134° with decomposition. Hofmann has previously prepared the same substance by the action of sulphuretted hydrogen on phenylcarbonylamine (*Ber.*, x, 1095, 1238). Ethenyl-diphenylamidine in a similar manner yields aniline, and probably *acetothianilide.*

By heating the amidines with carbon bisulphide at 100—120° a thiocyanogen-compound and a substituted thiamide are obtained; in this way benzenylmonophenylamidine gives *benzothianilide* and *benzenylmonophenylamidine thiocyanate*, thus:—

$$2C_6H_5(NH.C_6H_5)C{=}NH + CS_2 = C_6H_5.CS.NH(C_6H_5) + C_{13}H_{12}N_2.CNSH.$$

Under similar circumstances benzenyldiphenylamidine gives benzothianilide and phenylthiocarbimide—

$$C_6H_5(NH.C_6H_5)C{=}N(C_6H_5) + CS_2 = C_6H_5.NCS + C_6H_5.CS.NH(C_6H_5),$$

whilst benzenylisodiphenylamidine and carbon bisulphide yield *benzenylisodiphenylamidine thiocyanate* and *benzodiphenylthiamide*—

$$C_6H_5.CS.N(C_6H_5)_2.$$

The former of these bodies crystallises from a mixture of alcohol and benzene in dark-yellow prisms (m.p. 151°).

In a similar manner the author has prepared *acetodiphenylthiamide* from ethenylisodiphenylamidine. It melts at 111°, is easily soluble in ether, benzene, and alcohol, and but little soluble in water.

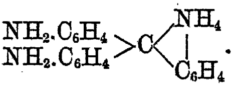
Acetothiamide, $CH_3.CS.NH_2$, is obtained by the repeated action of sulphuretted hydrogen on acetonitrile. It is very easily soluble in water and in alcohol, but less so in ether. It melts at 108°, and is completely decomposed by gentle warming with acids or alkalis. With iodine and silver nitrate it behaves like phenyl-aceto-thiamide, sulphur, and silver sulphide respectively being precipitated. Mercuric chloride with excess of acetothiamide gives a white precipitate crystallising in needles, which on warming are decomposed, yielding mercuric sulphide; with excess of mercuric chloride the precipitate is amorphous, and is not changed on warming. On treatment with zinc and hydrochloric acid, acetothiamide evolves sulphuretted hydrogen.

The author next describes the action of nascent hydrogen on thiamides, an account of which has already appeared in this Journal (1877, ii, 88, from *Ber.*, x, 36).

Phenylacetothiamide combines directly with ethyl bromide and methyl iodide to form the compounds, $C_8H_9NS.CH_3I$, m.p. 139°, and $CgN_9NS.C_2H_5Br$, which latter forms white or yellow easily decomposible needles, m.p. 130°.

Phenylacetothiamide likewise combines with benzaldehyde with elimination of water, forming a viscid oil, which gives with platinum chloride a brownish-yellow precipitate. T. C.

Rosaniline. By E. and O. FISCHER (*Deut. Chem. Ges. Ber.*, xi, 1079—1082).—By oxidising a glacial acetic acid solution of trinitrotriphenylmethane with chromic acid, a white crystalline trinitro-carbinol, $C_{19}H_{12}(NO_2)_3OH$ (m. p. 171—172°), is formed, which on treatment with zinc-dust yields pararosaniline, and finally leucaniline. This shows that rosaniline is either triamido-triphenyl carbinol or an anhydride of that body. The formula for pararosaniline is—



$$\begin{matrix} NH_2.C_6H_4 \\ NH_2.C_6H_4 \end{matrix} > C < \begin{matrix} NH_4 \\ | \\ C_6H_4 \end{matrix}.$$

The triphenylmethane derivative, $C_{23}H_{26}N_2$, prepared from benzaldehyde and dimethylaniline (*Ber.*, x, 1624) yields, on oxidation, formic aldehyde and a green colouring matter belonging to the rosaniline group.

The diazo-compound of hydrocyanopararosaniline forms a well crystallised chloride, sparingly soluble in alcohol. It is decomposed by boiling with alcohol; nitrogen and aldehyde are given off, and a non-nitrogenous acid and an indifferent nitrogenous compound are formed. The latter is perhaps triphenylmethane cyanide. W. C. W.

Aniline Black. By R. NIETZKI (*Deut. Chem. Ges. Ber.*, xi, 1093—1102).—The author ascribes to aniline black the formula $C_{30}H_{25}N_5$, to its hydrochloride, $C_{30}H_{25}N_5.2HCl$, and he represents the formation of the blue compound, $C_{36}H_{29}N_5$ (*Ber.*, ix, 1168), by treating aniline black with aniline, by the following equation:—

$$C_{30}H_{25}N_5 + C_6H_7N = C_{36}H_{29}N_5 + NH_3.$$

Aniline black yields a pale grey acetyl-compound, $C_{30}H_{23}N_5(C_2H_3O)$, insoluble in aniline and in concentrated sulphuric acid.

The bluish-violet base, with which crude aniline black is always mixed, can be prepared by the oxidation of orthotoluidine salts. Its empirical formula is C_7H_7N, and it is soluble in chloroform, in alcohol, and in aniline. The addition of an acid to the chloroform solution throws down a green salt. Paratoluidine does not yield analogous compounds.

By the reduction of aniline black with tin and hydrochloric acid, or with concentrated hydriodic acid and phosphorus, a resinous product is formed, from which, after treatment with alcohol, ether extracts paradiamidobenzene and diamidodiphenylamine, $NH_2.C_6H_4.NH.C_6H_4.NH_2$. The bases are separated by the sparing solubility of diamidodiphenylamine sulphate in cold water.

Diamidodiphenylamine is deposited from a hot aqueous solution in colourless feathery scales (m. p. 155°), which redden on exposure to the air. Its *acetyl* compound, $C_{12}H_{11}N_3(C_2H_3O)_2$, forms colourless needles (m. p. 239°), soluble in alcohol and glacial acetic acid, sparingly soluble in water. The salts of diamidodiphenylamine are all very soluble in water. Its sulphate, suspended in water and treated with nitrous acid, dissolves entirely, being converted into a diazo-compound. The sulphate separated in the crystalline state by the addition of alcohol and ether is easily soluble. This sulphate when boiled with alcohol was easily decomposed, yielding diphenylamine.

The aniline black which is not turned green by acids, and which is prepared by treating ordinary aniline black with potassium dichromate, contains 8 per cent. of CrO_3, and the author considers it to be merely the chromate of the aniline black. W. C. W.

Synthesis of Benzoic, Benzene-sulphinic, and Benzoylbenzoic Acids. By C. FRIEDEL and J. M. CRAFTS (*Compt. rend.*, lxxxvi, 1368—1371).—The authors find that benzoic acid is produced in small quantity on passing a current of perfectly dry carbonic acid gas through a mixture of aluminium chloride and benzene heated nearly to the boiling point of the latter. This reaction is attended by the evolution of hydrochloric acid, and is explained by the following equations:—

$$C_6H_5Al_2Cl_5 + CO_2 = C_6H_5.CO_2.Al_2Cl_5.$$
$$C_6H_5.CO_2.Al_2Cl_5 + H_2O = C_6H_5.COOH + Al_2Cl_5(OH),$$

the compound $C_6H_5Al_2Cl_5$ playing a part analogous to sodium ethyl in Wanklyn's synthesis of sodium propionate.

Sulphurous anhydride passed into a mixture of benzene and aluminium chloride acts much more energetically, giving rise to an analogous compound, benzene-sulphinic acid, $C_6H_5.SO_2H$. In a similar manner phthalic anhydride reacts on benzene in presence of aluminium chloride, yielding β or orthobenzoylbenzoic acid, $C_6H_5.CO.C_6H_4.COOH$; whilst with acetic anhydride benzene yields acetophenone as follows:—

$$C_6H_6 + (C_2H_3O)_2O = C_6H_5.CO.CH_3 + C_2H_3O.OH.$$

P. P. B.

Ethereal Oil of Thymus Serpyllum. By E. BURI (*Arch. Pharm.* [3], xii, 485—489).—*Properties of the Oil.*—Golden yellow, neutral, lævorotatory; a column of 100 mm. = 20·4° in the sodium light.

Fractional Distillation.—The oil began to boil at 180°, the temperature rising very rapidly to 350°. The following portions were collected separately.

(1.) 180—204°, very mobile, bright yellow.
(2.) 204—220°, the same, still brighter yellow.
(3.) 220—350°, less mobile, darker yellow.
(4.) Above 350°, still less mobile, greenish-yellow.

Finally a thick liquid oil came over, probably a decomposition-product. The following deviations were obtained:—

(1.)	A column 50 mm. long	....	—4·5°
(2.)	„ „	....	—5·2°
(3.)	„ „	....	—4·9°
(4.)	„ „	....	—2·9°

A few drops of water which were distilled over with the oil showed an acid reaction.

Acid obtained by Distillation.—All the fractions were shaken up repeatedly with water, the acid water was neutralised with baryta-water, evaporated, and finally placed over sulphuric acid. The syrupy liquid solidified to a crystalline mass. The acid by analysis of the silver salt gave results agreeing with the formula of argentic acetate, a very small quantity of an acid higher than acetic acid being also present.

With potassium bisulphite no crystalline compounds could be formed.

Phenols.—By treating the above fractions with potash solution, acidifying with sulphuric acid, and shaking up with ether, &c., in the usual way, an oil was ultimately obtained which was completely soluble in potash. Its boiling point was not constant. The following two oils were separated. By treating the oil with potash, agitating the alkaline solution with ether, and distilling, a colourless, strongly refracting oil was obtained, similar in smell to thymene, solidifying at —10°. Its weak alcoholic solution gave with ferric chloride a yellowish-green colour. By acidifying the aqueous alkaline solution and shaking it with ether, a few drops of an oil were obtained by distillation, which had a yellow colour, and gave an intense brownish-violet coloration with ferric chloride. About 3 per cent. of the former oil was found in wild thyme oil.

Sulpho-acids of the Colourless Phenol.—By treating a portion of the colourless phenol body with an equal weight of concentrated sulphuric acid at 60°, a red crystalline mass was obtained, similar in properties to the sulphonic acid obtained from thymol under the same conditions. The potash salt forms a colourless transparent mass, showing no indications of crystallisation: the lead salt was less amorphous, while the corresponding salts of thymol crystallise very readily. The characteristic blue coloration which salts of thymol-sulphonic acid give with ferric chloride was noticed with the above salts.

Quinone Bodies.—By distilling the lead and the potassium salt of the sulphonic acid with peroxide of manganese and sulphuric acid, a yellow crystalline body came over with the water, which was insoluble in the latter, and had a melting point of 45°.

In conclusion it is mentioned that the following plants are at present known to contain thymol as constituent in their ethereal oils:—*Thymus vulgaris*, L. (Neumann), *Monarda didyma*, L. (Brunn), *Monarda punctata*, L. (Arppe). Doveri examined in 1847 the crystallised portion of thymene, which Lallemand recognised as thymol. Stenhouse and Haines prepared thymol from *Ammi copticum*, L. (*Phychotis ajowan*, DC., and *Phychotis coptica*, DC.). D. B.

Preparation of Quinone. By R. NIETZKI (*Deut. Chem. Ges. Ber.*, xi, 1102—1104).—Powdered potassium dichromate is added to a cold mixture of 1 part of aniline, 8 of sulphuric acid, and 30 of water, until the precipitate of aniline black which is first formed redissolves, giving a brown solution. About 2½ parts of potassium dichromate are required for this purpose. If the process is now interrupted by the addition of a sulphite, hydroquinone is obtained, but in order to prepare the quinone it is necessary, after adding potassium dichromate (1 part) again, to leave the mixture at rest for some hours, and then heat it to 35°. The quinone is extracted by agitation with ether, as by this means 68 per cent. of the theoretical yield of quinone is obtained, whilst it is comparatively small if the quinone is distilled off in a current of steam. Quinone separates out from the ethereal solution in golden scales, which generally contain traces of quinhydrone. The mother-liquor from the quinone may be worked up for hydroquinone.

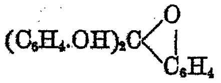
Toluquinone can be prepared from orthotoluidine by a similar process. W. C. W.

Rosolic Acid and Rosaniline. By H. CARO and C. GRAEBE (*Deut. Chem. Ges. Ber.*, xi, 1116—1123).—Aurin or pararosolic acid, prepared from phenol or from pararosaniline, is precipitated by hydrochloric acid from a hot alkaline solution in reddish-yellow slender needles, which dissolve in the dilute boiling liquid, and separate out on cooling. Under similar conditions rosolic acid from rosaniline, $C_{20}H_{16}O_3$, never forms needles, but it melts to green, metallic resinous drops, which slowly solidify.

Triacetylleucorosolic acid melts at 148—149°; *triacetylaurin* melts at 138—139°; both compounds crystallise in long colourless prisms, which are insoluble in water, but dissolve sparingly in cold, and readily in hot alcohol and ether.

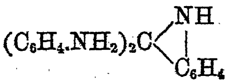
Triacetylhydrocyanorosolic acid melts at 143°, and the corresponding aurin derivative, which crystallises in colourless prisms insoluble in water and sparingly soluble in alcohol, melts at 193—194°.

The authors represent the composition of aurin, pararosaniline, and rosolic acid by the following formulæ:—



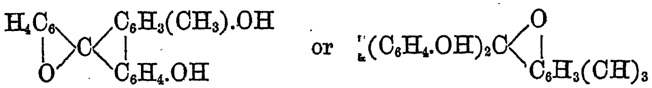
$$(C_6H_4.OH)_2C{<}\overset{O}{\underset{C_6H_4}{|}}$$

Aurin.



$$(C_6H_4.NH_2)_2C{<}\overset{NH}{\underset{C_6H_4}{|}}$$

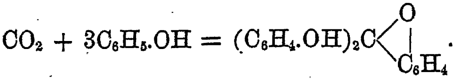
Para-rosaniline.



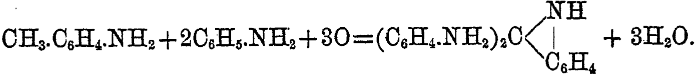
$$\begin{array}{l}H_4C_6 \\ | \\ O\end{array}\!\!>\!C\!<\!\begin{array}{l}C_6H_3(CH_3).OH \\ | \\ C_6H_4.OH\end{array} \quad \text{or} \quad (C_6H_4.OH)_2C\!<\!\begin{array}{l}O \\ | \\ C_6H_3(CH)_3\end{array}$$

Rosolic acid.

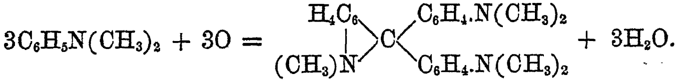
The former of the two formulæ for rosolic acid is regarded as the more probable. The following equations represent (1) the formation of aurin from phenol and oxalic acid, (2) the oxidation of a mixture of aniline and paratoluidine to pararosaniline, (3) the conversion of dimethylaniline to methyl violet, and (4) the formation of pararosaniline from triamidotriphenylmethane (leucopararosaniline).

(1.) 

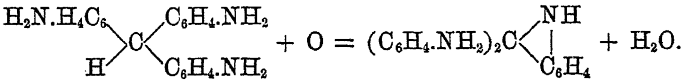
$$CO_2 + 3C_6H_5.OH = (C_6H_4.OH)_2C\!<\!\begin{array}{l}O \\ | \\ C_6H_4\end{array}.$$

(2.) 

$$CH_3.C_6H_4.NH_2 + 2C_6H_5.NH_2 + 3O = (C_6H_4.NH_2)_2C\!<\!\begin{array}{l}NH \\ | \\ C_6H_4\end{array} + 3H_2O.$$

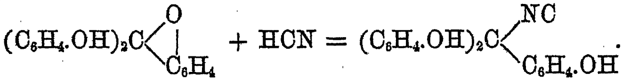
(3.) 

$$3C_6H_5N(CH_3)_2 + 3O = \begin{array}{r}H_4C_6 \\ | \\ (CH_3)N\end{array}\!\!>\!C\!<\!\begin{array}{l}C_6H_4.N(CH_3)_2 \\ \\ C_6H_4.N(CH_3)_2\end{array} + 3H_2O.$$

(4.) 

$$\begin{array}{r}H_2N.H_4C_6 \\ \\ H\end{array}\!\!>\!C\!<\!\begin{array}{l}C_6H_4.NH_2 \\ \\ C_6H_4.NH_2\end{array} + O = (C_6H_4.NH_2)_2C\!<\!\begin{array}{l}NH \\ | \\ C_6H_4\end{array} + H_2O.$$

The new formula explains why aurin yields a trioxy-derivative with hydrocyanic acid—



$$(C_6H_4.OH)_2C\!<\!\begin{array}{l}O \\ | \\ C_6H_4\end{array} + HCN = (C_6H_4.OH)_2C\!<\!\begin{array}{l}NC \\ \\ C_6H_4.OH\end{array}.$$

Aurin forms with acetic anhydride the compound $C_{19}H_{14}O_3.(C_2H_3O)_2O$, which crystallises in colourless plates (m. p. 159—160°).—It is insoluble in water, sparingly soluble in cold, but freely in hot alcohol. This derivative decomposes easily, yielding aurin, *e.g.*, from its solution in alcohol and caustic soda, hydrochloric acid precipitates aurin. A similar change is produced by cold strong sulphuric acid.

W. C. W.

Action of Bromine Water and of Nitrous Acid on Phenyl-Glycocine. By P. SCHWEBEL (*Deut. Chem. Ges. Ber.*, xi, 1131—1133).—*Tribromophenyl-glycocine*, $NH(C_6H_2Br_3).CH_2.COOH$, is formed by gradually adding bromine-water to a dilute aqueous solution of phenylglycocine until the white precipitate which is first obtained begins to turn yellow. It is soluble in boiling alcohol and glacial acetic acid.

Nitrosophenylglycocine, $N(NO)(C_6H_5).CH_2.COOH$, or

$$N(C_6H_5)(C_2H_3O_2).NO,$$

separates out in long yellow needles when potassium nitrite is added to a solution of phenylglycocine in sulphuric acid. It is soluble in alcohol, ether, and in hot water, but the solutions decompose on boiling. It melts at 105° with decomposition. W. C. W.

Solubility of the three Oxybenzoic Acids and of Benzoic Acid in Water. By H. Ost (*J. pr. Chem.* [2], xvii, 228—234).—Strong litre flasks were filled with the hot solution of the acids, and after cooling were loosely closed and surrounded with ice for several days. After the deposition of the crystals the amount of acid in solution was estimated by titration. The correct solubilities at 0° were found to be salicylic acid 1 : 1050—1 : 1100, benzoic acid 1 : 640, paroxybenzoic acid 1 : 580, oxybenzoic acid 1 : 265. All four acids need much longer time for the complete deposition of crystals when the solutions are dilute than when they are concentrated.

In the case of potassium nitrate and chlorate, and of sodium chloride, supersaturation was found to take place only to the most limited extent, and only in cases where the amount of crystals deposited was very small. According to Meyer (*Ber.*, 1875, 850), a rapid and complete deposition of crystals can be obtained only by constant agitation of the hot solution until it becomes cool. G. T. A.

Phenol-dicarbonic Acids and Oxytrimesic Acid. By H. Ost (*J. pr. Chem.* [2], xvii, 282—285).—Reimer states (*Ber.*, x, 1563, and xi, 793) that he obtained, in addition to other acids, a second (β-) phenol-dicarbonic acid, by the introduction of the formyl group into phenol, and oxidation of the first formylated compound produced. He also states that the author's oxytrimesic acid is a mixture of this β-phenol-dicarbonic with pure oxytrimesic acid. The author maintains that his oxytrimesic acid is pure. He cannot obtain β-phenol-dicarbonic acid by the action of carbonic acid on phenol and sodium, unless some slight traces of a second acid found in the mother-liquor when purifying some oxytrimesic acid consisted of the body in question, nor has he been able to obtain an oxytrimesic acid which does not colour ferric salts. G. T. A.

Synthesis of Phthalic Acid. By A. Guyard (*Bull. Soc. Chim.* [2], xxix, 247—250).—It was known that oxygen easily unites with benzene to form phenol, and that phenol absorbs carbonic anhydride, forming salicylic acid. The author has discovered that salicylic acid in a similar manner combines with carbon monoxide to form phthalic acid.

This synthesis may be effected in two ways. The first consists in heating a mixture of sulphuric acid and potassium ferrocyanide with salicylic acid, and when the reaction is ended, treating the resulting mass with ether, which extracts the phthalic acid; the second, in heating a mixture of sulphuric acid and formic acid with salicylic acid until gas is no longer disengaged. The mass is extracted with ether, which on evaporation yields perfectly pure phthalic acid easily recognised and identical with the phthalic acid from naphthalene.

Synthesis of Phthalic Acid from Resorcin and Carbon Monoxide.—The author finds that resorcin combines readily with carbon monoxide to form phthalic acid. But as an excess of resorcin is always present, the acid unites with it and forms fluoresceïn. The synthesis of phthalic acid and fluoresceïn are therefore realised simultaneously, nothing but fluoresceïn being obtained.

Synthesis of Phthalic Acid and Fluoresceïn from Salicylic Acid, Resorcin, and Oxalic Acid.—When salicylic acid or resorcin is heated with oxalic acid and sulphuric acid, that is to say, with a mixture yielding carbonic acid and carbon monoxide simultaneously, neither phthalic acid nor fluoresceïn is formed. But when salicylic acid or resorcin is heated with a mixture of oxalic acid and glycerin, that is, with a mixture yielding carbon dioxide in the first phase of the operation and carbon monoxide in the second, carbon dioxide is disengaged freely, and phthalic acid or fluoresceïn appears as soon as the mixture furnishes carbon monoxide.

These syntheses prove that phthalic acid is the point of convergence of the benzene and naphthalene series, being derived from the one by construction, from the other by destruction.

Synthesis of Phthalic Acid from Benzoic Acid.—Phthalic acid is easily transformed into benzoic acid; the reverse reaction is on the contrary very difficult to realise, although easily expressed by equation. However, by heating cautiously a mixture of benzoic acid, bicarbonate of soda, and resorcin, and treating the resulting mass with water, a solution is obtained presenting all the characteristics of fluoresceïn.

Phthalic acid was also obtained by allowing a mixture of benzyl chloride, C_7H_7Cl, perchlorethane, C_2Cl_6, and nitric acid to stand for a long time. F. J. L.

Tannin and Bitter Principle of Hops. By C. Etti (*Dingl. polyt. J.*, ccxxviii, 354—357).—The substance named "lupulo-tannic acid" (*ibid.*, ccxxvii, 491) by the author does *not* precipitate gelatin; if, however, it is dried at 120—130°, it changes from yellowish-white to red, loses water, and when dissolved in very dilute alcohol, *precipitates gelatin completely* just like ordinary tannin.

On heating the yellowish alcoholic solution of the original tannin on the water-bath, it becomes red, and on evaporation, a dark red residue remains which also precipitates gelatin when again dissolved in dilute alcohol. The author calls this "phlobaphen."

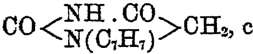
Analysis gives the same composition for this as for the red compound obtained by heating the lupulo-tannic acid at 120—130°, each having the formula $C_{50}H_{46}O_{25}$; and they may be supposed to result from the expulsion of a molecule of water from two molecules of tannic acid of the formula $C_{25}H_{24}O_{13}$.

The coarsely powdered hop flowers are placed in an extraction apparatus, and after being freed from resin and bitter-principle as much as possible, the mass is extracted with 20 per cent. alcohol. On evaporating to a small bulk and cooling, a red precipitate of phlobaphen is formed: this is dissolved in 90 per cent. alcohol, evaporated to dryness, and heated to 120—130°. If it tastes bitter, the bitter principle may be removed by ether. Phlobaphen is easily soluble in alkalis, and is precipitated unchanged by dilute mineral acids. On boiling the freshly precipitated and not previously heated phlobaphen with dilute mineral acids it is decomposed, glucose and one molecule of water being split off.

As the phlobaphen is easily prepared, is constant in composition, and precipitates gelatin solution completely, it may be estimated quantitatively like tannin, and may be used in standardising the solution employed.

An ethereal extract of hop flowers contains, besides an essential oil, chlorophyll, a crystallised white and an amorphous brown resin, to which the bitter principle adheres. After driving off the ether, 90 per cent. alcohol dissolves brown resin and the bitter principle, which may be separated from each other by adding water as long as the resin continues to be precipitated. Repeated solution in alcohol and dilution with water frees the resin from the bitter principle. The aqueous solution is evaporated in a vacuum over sulphuric acid, the amorphous residue dissolved in 90 per cent. alcohol, again evaporated, and so on repeatedly, until well-formed extremely bitter, colourless crystals are obtained. The crystals are completely soluble in water. These experiments oppose the idea that the "bitter resin" of hops can be dissolved in water only with the aid of sugar, tannic acid, gum, ethereal oil, &c. The brown amorphous resin and the bitter principle of hops are two fundamentally different substances. J. T.

Aromatic Hydantoïns. By P. SCHWEBEL (*Deut. Chem. Ges. Ber.*, xi, 1128—1131).—Several bodies are produced, when equivalent quantities of urea and paratolyl-glycocol are fused together. Hot alcohol extracts from the fused product *tolylhydantoic acid* and *monotolylcarbamide*, leaving *tolylhydantoïn* and a crystalline substance (m. p. 174°) undissolved. On evaporating the alcoholic extract, tolylhydantoic acid, $NH_2,CO.N(C_7H_7).CH_2.COOH$, is obtained as a white powder, insoluble in cold water and cold alcohol, and sparingly soluble in boiling alcohol. It decomposes at 200° without melting, and is precipitated from its solution in ammonia by acids. On adding hydrochloric acid to the mother-liquor from the tolylhydantoic acid, the monotolylcarbamide separates out. It is deposited from a solution in hot alcohol in silvery needles, which are insoluble in water and ammonia, and are not attacked by acids or alkalis. It is decomposed at 200°. It is not identical with Sell's compound (*Annalen*, cxxvi, 158). Tolylhydantoïn,



$CO<\genfrac{}{}{0pt}{}{NH\,.\,CO}{N(C_7H_7)}>CH_2$, crystallises in colourless needles (m. p. 210°) insoluble in cold water but soluble in alcohol. W. C. W.

Ammonia Derivatives of Isatin. By E. v. SOMMARUGA (*Deut. Chem. Ges. Ber.*, xi, 1082—1085).—This is a continuation of the author's research on the action of ammonia on isatin under pressure (*Annalen*, cxc, 367—384).

Di-amido-isatin, $C_{16}H_{12}N_4O_2$, forms the following salts; the *hydrochloride*, $C_{16}H_{12}N_4O_2.HCl$, is a yellow powder, consisting of microscopic needles; the *nitrate*, $C_{16}H_{12}N_4O_2.HNO_3$, resembles the preceding salt; the *sulphate*, $C_{16}H_{12}N_4O_2.H_2SO_4$, crystallises in light yellow needles; and the *chromate*, $C_{16}H_{12}N_4O_2.H_2CrO_4$, is an orange coloured powder.

The diamide is reduced by sodium-amalgam forming the compound, $C_{16}H_{13}N_3O_3$, which is insoluble in water, but crystallises from alcohol in small colourless needles. The *sodium* derivative of this body, $C_{16}H_{12}NaN_3O_3$, forms long colourless needles very soluble in water and the *potassium* compound, $C_{16}H_{12}KN_3O_3$, crystallises in silvery needles.

Oxydi-imido-di-amido-isatin, $C_{16}H_{14}N_6O_3$, yields a nitroso-product, which has not yet been obtained in the pure state; it also forms a series of salts which are characterised by the intense bluish-red fluoresence of their solutions. The nitrate, $C_{16}H_{14}N_6O_3.HNO_3$, and the sulphate, $C_{16}H_{14}N_6O_3.H_2SO_4$, both crystallise in needles. On reduction with sodium amalgam, the following reaction takes place—

$$C_{16}H_{14}N_6O_3 + 5H_2 = C_{16}H_{16}N_4O_2 + H_2O + 2NH_3.$$

By oxidising the product of the reaction, which is possibly the diamide of hydriodic acid, with potassium dichromate and sulphuric acid, di-imido-hydrindin-carbonic acid, $C_{16}H_{12}N_4O_4$, is obtained.

Desoxyimido-isatin yields an amorphous isomeride of mon-amidodihydro-isatin, when it is submitted to the action of sodium amalgam: $C_{16}H_{11}N_3O_2 + H_2O = C_{16}H_{13}N_3O_3$. The same reaction takes place when it is heated under pressure with water or an alkaline solution.

W. C. W.

Remarks on Violaceïn and Eupittone. By C. LIEBERMANN (*Deut. Chem. Ges. Ber.*, xi, 1104—1106).—This paper is not of general scientific interest, being a correction of a statement by Grätzel as to the identity of the two substances. W. C. W.

On the Volatile Oil of the Leaves of Myrcia acris. By G. F. H. MARKOE (*Pharm. J. Trans.* [3], viii, 1005).—Bay leaves when distilled with water, yield a heavy and a light oil: the light oil passing over in the first portion. It is believed that the heavy oil is identical with eugenic acid; it has a sp. gr. of 1·055 at 15·5°.

The light oil, which is a clear colourless liquid, has a sp. gr. of ·829 at 25°, and of ·8356 at 15·5°, and is believed to be a terpene. On distilling these oils with water, a residue remains in the still, which is of a dark colour, and appears to be a resin formed by the oxidation of the eugenic acid. E. W. P.

Researches on Essence of Valerian. By G. BRUYLANTS (*J. Pharm. Chim.* [4], xxvii, 349—353).—The oil of valerian when fresh is slightly acid, the colour varies according to the kind of valerian used for its preparation: green when made from *Valeriana sylvestris*, and yellow when roots grown in a marshy ground are employed in its manufacture. The fresh oil is without smell, but if left in contact with the air, it becomes resinous and acquires a fœtid odour, owing to the formation of valeric acid. The oil varies according to the age of the root from which it is extracted; when prepared from old roots it is much more acid and contains more resin than that from fresh roots.

The oil begins to boil at about 120°, but the temperature rapidly rises to 160°, when the distillation continues regularly to about 350°. A blackish resinous residue is left in the retort, having a strong smell of leather. When the oil is freshly prepared, it contains about 5 per cent. of this resinous substance. After a number of distillations (20), the following fractions were obtained:—

The first	portion boiling	between	155°	and	165°
second	,,	,,	205	,,	210
third			220		225
fourth			230		235
fifth			240		245
sixth			285		290

Excepting the first and last fractions, the others were not obtained in a state of purity on account of the closeness of their boiling points, but nevertheless they were identified by their decomposition products.

The portion boiling at 155—165° contained a few drops of an acid body which was deposited on allowing the specimen to rest for some time, when it was collected, and a barium salt prepared from it. This salt on boiling with silver nitrate gave a black precipitate of metallic silver, and with lead acetate a white precipitate of formate of lead was produced. After boiling the barium salt with silver nitrate and filtering, the filtrate on cooling gave crystals yielding on analysis 58·02 per cent. of silver; this is fairly near the amount required (for formate), but might also indicate the presence of a mixture of acetic and valeric acids; the author is inclined to regard the latter as the correct view. There was not sufficient material to make further experiments.

The oily liquid—boiling from 155—165°—was distilled several times over sodium to free it from traces of substances containing oxygen, valerianic acid, &c. The vapour-density for $C_{10}H_{16}$ was: 136 calculated, 138 found; the molecular weight 4·69 calculated, 4·76 found; the boiling point was 155—157°. After boiling for some hours with iodine, a large quantity of hydriodic acid was evolved, with formation of a hydrocarbon, $C_{10}H_{14}$, methylpropylbenzene, identified by its oxidation-products, toluic and terephthalic acids. The terpene absorbs a large quantity of hydrochloric acid, giving a crystalline product.

The author promises another communication on the subject.

R. C. W.

Cynanchol. By O. Hesse (*Liebig's Annalen*, cxcii, 182—185). By a process of very careful fractional crystallisation from 93 per cent. alcohol, cynanchol was split up into two substances, for which the author proposes the names of *cynanchocerin* and *cynanchin* respectively. The former substance crystallises in needles, the latter in tabular forms. A table of the qualitative reactions of these two bodies, and also of *echicerin* and *echitin*, is annexed to the original paper.

M. M. P. M.

Euphorbone. By O. Hesse (*Liebig's Annalen*, cxcii, 193—195). —Euphorbone was obtained from euphorbium by extracting with petroleum ether, and allowing the solution to evaporate spontaneously. On treating the semi-crystalline residue with hot alcohol, and, after the solution had cooled somewhat, pouring off from resin which was deposited, crystals separated which were purified by crystallisation from acetone.

From his own analyses and those of Rose, Dragendorff, &c., the author deduces the formula, $C_{15}H_{24}O$, for euphorbone. This substance is isomeric with lactucone; or perhaps it may possess the double formula, $C_{30}H_{48}O_2$, and so be an isomeride of echicerine. Euphorbone melts at 113—114°. For a chloroform solution the rotatory power of euphorbone is $(\alpha)_D = + 18·8$ at 15°; and for an ethereal solution $(\alpha)_D = + 11·7°$.

M. M. P. M.

Active Principle in Persian Insect Powder. By ROTHER (*Chem. Centr.*, 1878, 367).—The active substance in this powder is an acid, or more properly a glucoside, which the author calls *persicin*. It is of a brown colour, uncrystallisable, smells like honey, and is decomposed by heating with hydrochloric acid into sugar and *persiretin*. With potash it forms a neutral amorphous, and an acid crystallisable salt. Persiretin behaves like an acid, it has a brown colour, is but sparingly soluble in water, but dissolves in alcohol and in alkalis with a brown colour. The above powder contains also an oily resinous acid called *persicein*. It has the smell of the powder and a bitter taste, dissolves in ether, alcohol, benzene and alkalis, not in chloroform. No alkaloïds could be detected in the powder, although Bellesme states that he has obtained an alkaloïd from it, which is said to possess all the toxical properties of the powder in a high degree, whilst the volatile oil is quite inactive.

D. B.

Meconoisin, a New Derivative from Opium. By T. and H. SMITH (*Pharm. J. Trans.* [3], viii, 981).—The mother-liquor after the separation of meconin, when allowed to stand some days, deposits crystals, which, being drained and washed with alcohol, dissolve in water, recrystallising from it in large leaf-shaped crystals: when purified by further recrystallisations, they are colourless, soluble in 27 parts of cold water, and to almost any extent in hot water, forming a syrupy solution. Meconoisin, $C_8H_{10}O_2$, melts at 88°, and when heated with slightly diluted sulphuric acid, yields, when partly evaporated, a beautiful green colour, whereas meconin becomes purple under the same circumstances.

E. W. P.

The Quinidine of Henry and Delondre. By O. HESSE (*Liebig's Annalen*, cxcii, 189—193).—A short controversial paper as to the identity of Henry and Delondre's quinidine and the author's conchinine. The author's analyses of cinchona barks are as follows:—

	Rouge de mutis.	Jaune de mutis.	Rouge vif.	Rouge pâle.	Pitayo.
Quinine ..	0·00	0·96	1·33	1·26	0·77
Quinidine.	0·00	0·17	0·51	1·88	trace
Conchinine	0·00	trace	0·00	trace	0·21
Cinchonine	0·17	0·27	0·55	0·59	0·40
Quinamine	trace	0·00	0·00	0·00	0·00
Amorphous bases....	0·43	0·47	1·66	1·92	1·32
	0·60	1·87	4·05	5·65	2·70

He concludes that quinidine and conchinine are not identical.

M. M. P. M.

Alkaloïds of Sabadilla Seeds. By O. Hesse (*Liebig's Annalen*, cxcii, 186—188).—On the evidence of the published results of analyses by Weigelin, Merck, &c., the author regards the formulæ of the alkaloïds of sabadilla as follows:—

Sabadilline......	$C_{21}H_{35}NO_7$.
Sabatrine	$C_{26}H_{45}NO_9$.
Veratrine	$C_{32}H_{51}NO_9$.

M. M. P. M.

Note on the Alkaloïd Sophorine. By H. C. Wood (*Pharm. J. Trans.* [3], viii, 1047).—The beans of *Sophora speciosa* yield a liquid alkaloïd whose chloride is stable, and crystallises easily: with ferric chloride a deep-red colour is produced. As a poison, three grains hypodermically injected did not affect a dog very seriously, but killed a cat in a short time. E. W. P.

Remarks on Barth's "Research on Invertin." By E. Donath (*Deut. Chem. Ges. Ber.*, xi, 1089—1091).—This is merely a reply to Barth's criticisms on the author's investigation on invertin, and does not possess any scientific interest. W. C. W.

Researches on the Peptones. By A. Henninger (*Compt. rend.*, lxxxvi, 1464—1466).—The author obtained from fibrin-peptone by the action of a dehydrating agent (acetic anhydride) a substance which exhibited many of the properties of syntonin, but proved not to be identical with that substance. The researches described in the paper appear to indicate that the peptones result from the fixation of water on albuminoïd substances. They may be compared to acid amides, or rather to the uramic acids, albuminoïd substances being complex ureides. R. R.

Chemistry of Vegetable Physiology and Agriculture.

Effect of Frost on Flax Seeds. By F. Haberlandt (*Landw. Versuchs.-Stat.*, xxi, 357—361).—Linseed was steeped in water and then exposed to a low temperature for two days. It was found when frozen at −10° and then quickly thawed, that 83 per cent. germinated, but if slowly thawed only 79 per cent. Frozen at −24° and quickly thawed, 20 per cent. germinated, but when slowly thawed only 1 per cent. The plants grown from seed which had been frozen at −10·5° were found to be 44·8 per cent. longer than ordinary seed yielded. A second experiment on seed frozen at −10° gave an increase in length of 39 per cent. J. T.

Composition of Gases Contained in the Cells of Wood. By J. Boehm (*Landw. Versuchs.-Stat.*, xxi, 373—388).—The author concludes that:—

1. The gas, collected by boiling in water living branches containing

air only, is poor in oxygen, and always contains over 30 per cent. of carbonic anhydride, whilst fresh branches, killed by hot steam and then heated up to 90° in pure oxygen for 6 to 7 hours, form very little carbonic anhydride. These results seem to show that the inner cells are only slowly killed in the first case, owing to the low heat-conductivity of the wood, and that the contained oxygen is converted into carbonic anhydride during the process.

2. The best method for extracting the air is to seal one end of the branch, immerse it in water at a low temperature, and connect the other end with a Sprengel pump.

3. In consequence of the low tension of the air in the cells of living plants, only that portion is extracted which has been absorbed by the branch whilst being cut off. Only in one case had the air obtained approximately the composition of that in the living plants. The cells of Syringa in a frozen branch are almost impermeable to compressed air, whilst, when thawed, air easily permeates them.

4. Numerous analyses show that the total percentage of oxygen and carbonic anhydride obtained from thawed branches is always less than the amount of oxygen contained in the atmosphere. During slow experiments carbonic anhydride is always formed by internal respiration. The remarkable composition of the cell-gas bears some relation to its low tension, and is evidently a consequence of the relatively easy permeability of moist membranes for carbonic anhydride.

5. During the experiment a little air is absorbed and a little gas escapes.

6. In the first portions of gas extracted, the total percentage of oxygen and carbonic anhydride is always greater than in the following portions, and is greater than the oxygen contents of the atmosphere. It is in consequence of the relatively easy permeability of moist membranes for oxygen that this gas is absorbed in greater quantity by water than nitrogen is. The gas obtained from branches during the first five minutes often contained over 24 per cent. of oxygen.

7. Syringa branches which had hung for eight days during winter within a moistened cylinder, at an ordinary room temperature, gave very little gas, as was also the case with gas from thawed branches; the total percentage of carbonic anhydride and oxygen was always less than that of the atmosphere.

8. The gas obtained as quickly as possible from freshly cut willow branches in summer contained from 9 to 12 per cent. of carbonic anhydride, showing that the cell-gas of plants in active growth is rich in carbonic anhydride.

9. The gas obtained from the roots of willow plants always contains a total percentage of carbonic anhydride and oxygen less than that of the oxygen in the atmosphere. The cause of this must be that a part of the carbonic anhydride formed by the permeation of the air is carried away by the ascending sap-current. This agrees with the fact that gas extracted from the branches is richer in carbonic anhydride as the transpiration is more active. J. T.

Influence of Gypsum Solution on Soils. By W. Kalmann and F. Bocker (*Landw. Versuchs.-Stat.*, xxi, 349—355).—The authors undertook this investigation, partly because of the contradictory results obtained by other investigators, and partly to ascertain the influence of the state of concentration and time of working of the gypsum solution on the absorption of the lime, and also on the solubility of the bases and phosphoric acid contained in the soil. The soil was taken from land which had lain fallow the previous year, and received no manure. Only fine earth was used, of which the following is a mechanical analysis:—

29·47 parts	Gravel	26·18	
	Organic matter with it	—	3·29
24·93 "	Coarse sand	21·56	
	Organic matter with it	—	3·37
10·95 "	Fine sand	9·70	
	Organic matter with it	—	1·25
1·57 "	Clayey sand	1·38	
	Organic matter with it	—	0·19
32·19 "	Finest part	26·11	
	Organic matter with it	—	6·08
99·11 "		84·93	14·18

From the results of the experiments the authors conclude that:—

1. A soil absorbs more lime from a concentrated solution of sulphate than from a dilute one, but the amount is not proportional to the degree of concentration.

2. The amount of lime absorbed increases with the time during which the soil and solution are in contact, but the increase is not proportional to the time, and the influence of the time is very subordinate.

3. More magnesia and alkali is dissolved by gypsum solution than by distilled water. The more concentrated the solution the more of the above bases are dissolved, but the amount dissolved is not proportional to degree of concentration of the gypsum solution.

4. The amount of magnesia and alkali dissolved does not increase continually with the time of contact.

5. The gypsum acts more especially on the sodium compounds, as was found by Knop (*Kreislauf des Stoffes*, ii, 191).

6. The amount of lime absorbed is not equivalent to the more soluble bases removed; the agreement obtained by Heiden (*Düngerlehre*, ii, 444) appears to be accidental only.

7. Phosphoric acid is extracted both by water and by gypsum solution; the gypsum, however, has no influence on the quantity of acid passing into solution.

8. The time that the soil and solution were in contact had but little effect on the result.

J. T.

Distribution of Salts in the Soil. By H. Pellet (*Compt. rend.*, lxxxvi, 1201—1203).—Salts may be divided into two classes, according to their tendency to rise to the surface or to sink down into the soil. To ascertain to which class a substance belongs, a layer of [illegible] 16 centimeters deep, containing about 2 per cent. of the salt, is placed in a test-ube and 20 per cent. of water added. After 36 hours the column of sand is cut in two, and the amount of the salt determined in the upper and lower portion.

The following results were obtained:—

	Potassium.		Sodium.		Calcium.		Ammonium.	
	Upper.	Lower.	Upper.	Lower.	Upper.	Lower.	Upper.	Lower.
Carbonate	1·2	1·5	1·36	0·87	—	—	—	—
Sulphate	1·3	0·6	0·95	0·56	—	—	1·36 1·70	1·66 1·22
Chloride.	2·3 2·1	0·73 1·10	2·00	0·66	0·75	1·21	2·73	0·2
Nitrate..	2·1	0·90	1·65	0·82	3·03	0·946	1·31	1·85
Phosphate	2·2	1·01	1·29	0·45	2·045	1·545	2·4	0·73

There is not any appreciable difference in the quantity of magnesium salts occurring in the upper and lower layers.

The distribution of the salts is considerably affected by the nature of soil and by the rate of evaporation at the surface. Calcium superphosphate rises to the surface with such rapidity that there is a chance of its interfering with the germination of seeds.

W. C. W.

The Best Form of Nitrogenous Food for Barley. By P. HÄSSELBARTH (*Landw. Versuchs.-Stat.*, xxi, 363—371).—The investigation was undertaken to ascertain whether plants take up nitrogen equally well when presented as nitrates or as ammonia-compounds. Quartz sand specially purified was used as soil. Glass vessels were taken in each of which 12 barley-grains of an average weight of 45·9 mg. were sown, after a time the plants were reduced to six in each box. The boxes were prepared in pairs. In one series the nitrogen was added as calcium nitrate, in the second series as ammonium compounds without marl, in the third series as ammonium compounds with marl; the fourth series (19 to 22) was like the third, with the exception that no seeds were sown, the object being to determine the amount of nitrogen converted into nitric compounds. To each box the following substances were added:—

2	mg.	equivalents	KH_2PO_4
1	,,	,,	KCl
1·6	,,	,,	$MgSO_4$
5	,,	,,	$Fe_2O_3.3H_2O$.

The boxes in each pair agreed very well together, so that the average was taken. The results are given in Tables I and II. 23 shows the results obtained from a box to which no nitrogen at all was added.

TABLE I.

No. of the Box.	Milligram-equivalents.										
	KH_2PO_4.	KCl.	$MgSO_4$.	$Fe_2O_3 + 3H_2O$.	$Ca(NO_3)_2$.	$CaSO_4 + 2H_2O$.	$(NH_4)_2SO_4$.	$NH_4H_2PO_4$.	NH_4Cl.	NH_4NO_3.	40 gr. $CaCO_3$.
1 and 2	2	1	1·6	5	16	—	—	—	—	—	—
3 and 4, 11 and 12	2	1	1·6	5	—	16	16	—	—	—	40
5 and 6, 13 and 14	2	1	1·6	5	—	16	—	16	—	—	40
7 and 8, 15 and 16	2	1	1·6	5	—	16	—	—	16	—	40
9 and 10, 17 and 18	2	1	1·6	5	—	16	—	—	—	8	40
23	2	1	1·6	5	—	16	—	—	—	—	—

No. of the Box.	Dried Plant in Grams. (Average of two Boxes.)			Ash in Grams.		
	Grain.	Straw and Chaff.	Total.	Grain.	Straw and Chaff.	Total.
1 and 2	10·4800	10·2104	20·6901	0·186	0·386	0·572
3 and 4, 11 and 12..	10·0914	10·0057	6·6932 20·0971	0·160	0·525	0·398 0·685
5 and 6, 13 and 14..	5·1375	4·6381	1·0097 9·7756	0·156	0·550	0·707
7 and 8, 15 and 16..	9·4198	11·3879	20·8077	0·173	0·656	0·414 0·829
9 and 10, 17 and 18............	8·8526 11·9321	9·5166 13·6276	18·3692 25·5603	0·217 0·185	0·484 0·565	0·701 0·750
23	0·5110	0·7585	1·3995	—	—	—

TABLE II.

No. of Box.	Absolute Amount of Nitrogen. (Mean of two Boxes.)				Absolute Amount of Lime. Mean of two Boxes.		
	Grain.	Straw and Chaff.	Total.	Per cent. of added N.	Grain.	Straw and Chaff.	Total.
1 and 2.....	0·1607	0·0534	0·2141	95·56	0·010	0·062	0·072
3 and 4.....	—	—	0·1142	50·98	—	—	0·013
11 and 12....	0·1428	0·0708	0·2136	95·36	0·011	0·110	0·121
5 and 6.....	—	—	0·0344	15·38	—	—	—
13 and 14....	0·1032	0·0400	0·1432	63·91	0·003	0·038	0·041
7 and 8.....	—	—	0·0970	42·30	—	—	0·020
15 and 16....	0·1418	0·0815	0·2233	99·67	0·010	0·078	0·088
9 and 10....	0·1275	0·0705	0·1980	88·41	0·007	0·104	0·111
17 and 18....	0·1735	0·0587	0·2322	103·66	0·010	0·143	0·153

The greatest amount of nitrogen was taken up, and most dry substance was produced, when the nitrogen was added in the form of nitrates, or under such conditions that it could be converted into nitrates. Nearly the whole of the added nitrogen was taken up when calcium or ammonium nitrate was added, or when ammonium sulphate and chloride in marled soil were employed, whilst only about half the nitrogen was taken up when the soil was not marled. A larger quantity of lime also was taken up when the nitrogen was completely assimilated.

The amount of nitrogen converted into nitrate in the boxes 19, 20, 21 was found to be as follows:—

No.	Compound added.	Per cent. of N as nitrate.
19	$(NH_4)_2SO_4$ ·224 grams N	36·16
20	$NH_4H_2PO_4$ ·224 grams N	36·16
21	NH_4Cl ·224 grams N	51·78
22	Lost.	

J. T.

Analytical Chemistry.

Colorimeter for Quantitative Analysis. By A. R. LEEDS (*Chem. News*, xxxvii, 229).—The comparison tubes, each of which when filled to the depth of 6 inches contains 100 c.c., are arranged in a rack; and above them is an adjustable mirror which reflects light down through the tubes, through slits cut in a stage below, on to a second mirror. For ammonia the comparison is effected by a hollow glass prism filled with caramel solution and a small addition of aniline red. Above the prism in the comparator, a comparison tube with about 20 c.c. distilled water is placed. The comparison liquid is made of such a strength that the light, after traversing its greatest depth in the prism, shall give a tint corresponding to 10 centimilligrams of ammonia.

The acidity or alkalinity of potable waters may be determined by the aid of this instrument, using alizarin as an indicator and a centinormal solution of soda. The amount of carbon combined in iron or steel may also be easily determined, since the colour of the solution of the iron in nitric acid varies as the amount of carbon (Eggertz's method). E. W. P.

Determination of Nitrogen in Gas Analysis. By H. BUNTE (*Deut. Chem. Ges. Ber.*, xi, 1123—1127).—Instead of exploding the mixture of oxygen and hydrogen or hydrocarbon in a eudiometer by means of the electric spark, it is proposed to bring about the combination by passing a measured volume of the mixed gases over a small coil of palladium wire heated to redness. Full details for applying the method are given in the original paper. W. C. W.

Estimation of Manganese in Iron, Steel, &c. By V. DESHAYES (*Bull. Soc. Chim.* [2], xxix, 541—551).—This method consist in oxidising a solution of the nitrate, or nitrate and sulphate of manganese, with lead dioxide, and reducing the permanganic acid with a standard solution of sodium arsenite, prepared by dissolving 5 grams of arsenious acid in 10 grams of sodium carbonate, and diluting the solution to 1,500 c.c. This solution is used as a reducing agent in preference to a solution of mercurous nitrate.

A standard manganese solution is prepared by dissolving 1·109 gram of pure mangano-manganic oxide, Mn_3O_4, in 140 c.c. of sulphuric acid and 500 c.c. of water. 100 c.c. of hydrochloric acid are then added, and the whole boiled until the solution becomes clear. When cold it is made up to 4 litres. 5 c.c. of this solution correspond to 0·001 gram manganese.

To determine the strength of the reducing solution in terms of the standard solution, 5 c.c. of the latter are mixed with 20 c.c. of nitric acid and boiled with 4 grams of lead dioxide for a few minutes. 4 grams more of the dioxide are again added to the hot liquid, and the solution made up to 100 c.c. When the precipitate has settled the clear liquid is decanted and 50 c.c. titrated with the sodium arsenite.

Estimation of Manganese in Iron and Steel.—From 1·0 to 0·1 gram of the metal (according to the percentage of manganese) is dissolved in 20 c.c. of nitric acid and 20 c.c. of water; to the boiling solution, 4 grams of lead dioxide are added, and after continued boiling 4 grams of the oxide are again added, but without subsequent boiling, and the solution titrated with sodium arsenite. In a similar manner manganese in spiegeleisen, in manganese minerals, &c., may be estimated.

Full details are given in the paper, and the results show the accuracy which may be attained by the use of this method, whether in the estimation of large or of small quantities of manganese.

L. T. O'S.

Detection of Cellulose by Means of Phloroglucin. By R. v. WAGNER (*Dingl. polyt. J.*, ccxxvii, 173—174).—The observation lately made by J. Wiesner (ccxxvii, 397, and this vol., 612) that woody matter may be detected, *e.g.*, in paper, by means of phloroglucin and hydrochloric acid, is of great interest technologically. Some conditions must be borne in mind. The test succeeds with woody fibre in paper; on the contrary, it does not succeed with cellulose which has undergone the usual treatment by soda lye, bleaching, &c., of a cellulose manufactory. Raw shavings of coniferous woods give a violet colour with phloroglucin and hydrochloric acid.

In an earlier paper (*J. pr. Chem.*, lii, 451) the author observed that the yellow wood of *Maclura tinctoria* gave a deep red or violet colour when moistened with concentrated hydrochloric acid. There is nothing remarkable in this, considering the close relation existing between morintannic acid and phloroglucin. But there is something surprising in the fact that pine and fir should take a violet colour when moistened with concentrated hydrochloric acid (without addition of phloroglucin) and then exposed to sunlight.

The reaction of phenol with a splinter of resinous wood and hydrochloric acid, noticed by Runge, is, in spite of its uncertainty (*J. pr. Chem.*, li, 95), probably applicable in certain cases for the detection of woody matter. Wiesner's test is really a modification of Runge's: both result from the use of phenol, only Runge applied ordinary carbolic acid, whilst Weisner uses a triatomic phenol, phloroglucin.

J. T.

New Test for Phenol. By E. W. DAVY (*Pharm. J. Trans.* [3], viii, 1021).—The reagent employed for the detection of phenol is similar to that employed by the author for the detection of alcohol, and consists of a solution of one part molybdic acid in ten parts by weight of concentrated sulphuric acid. The method of using this reagent is simply to add three or four drops of it to one or two of the liquid under examination, placed on a white porcelain surface. If phenol be present, even to the small amount of $\frac{1}{350000}$ grain, a yellowish-brown coloration will be first produced, changing to purple; if phenol alone be employed, and not its aqueous solution, a dark olive, changing to blue, is produced, but not purple; all phenol solutions should therefore be diluted, unless they are already so, and to aid the reaction a heat not greater than 53° may be applied; but as some other organic substances will likewise, when heated with the molybdic reagent, produce a purple coloration, it is better to allow the reaction to take place at the ordinary temperature; at 100° the purple is destroyed, a blue being produced in its place. In point of delicacy the above test is surpassed only by Landolt's bromine test (formation of tribromophenol), but is more successful under circumstances which affect the bromine test. The reaction appears to be due to deoxidation of the molybdic acid, and not to oxidation of the phenol. It serves to detect phenol in creosote, as pure creosote produces only a reddish-brown tint. By distilling the creosote containing phenol with water, pure creosote passes over, first as an emulsion, later on the phenol passes over and may easily be detected. E. W. P.

Remarks on the Analysis of Crude Tartars. By A. Scheurer-Kestner (*Bull. Soc. Chim.* [2], xxix, 451—456).—Tartars frequently contain, besides potassium bitartrate, neutral calcium tartrate, which in some samples is found in large quantities: calcium sulphate is also occasionally present.

Estimation of Potassium Bitartrate.—This salt is generally estimated by means of a standard solution of potash or soda, or else the sample is calcined, and the residue, consisting of carbonates, titrated with standard acid. But this method cannot be relied on in the presence of calcium tartrate, unless a determination is made of the latter and deducted from the total alkali. Calcium sulphate also interferes by its action upon the potassium carbonate. In the absence of calcium salts, the titration of the residue after calcination gives exact results; but the direct estimation of the acid with standard alkali is liable to error, as some tartars, more especially lees, contain acid organic products other than tartaric acid. Therefore in the presence of calcium tartrate the calcined mass should be dissolved in water, and the solution titrated with standard acid; but even then an error will be introduced if calcium sulphate is present.

Estimation of Calcium Tartrate.—The following method gives good results. The tartar is calcined, dissolved in water, filtered, washed, and the filtrate titrated; the cream of tartar is then calculated from this estimation. The residue on the filter ($CaCO_3$) is also titrated, and calculated as calcium tartrate. Calcium sulphate should always be tested for, as it vitiates the results by being precipitated as calcium carbonate (when water is added to the calcined residue), and so finally calculated as calcium tartrate. In the presence of calcium sulphate, only an approximation can be made of the relative amount of potassium bitartrate and calcium tartrate, and even this is not possible when the sample contains other acid substances besides tartaric acid. But in the absence of such acid substances, by estimating the bitartrate with a standard solution of alkali, and the total tartaric acid (that combined with the calcium as well as the potassium) as calcium tartrate, the proportions of the salts originally present may be calculated. When, however, foreign acid substances are present, the author finds that the following process gives exact and concordant results.

The sample is dissolved in hydrochloric acid, filtered, and to the filtrate calcium chloride is added, and the tartaric acid precipitated as calcium tartrate by means of caustic soda, not in excess. To avoid the precipitation of calcium hydrate, ammonia is used to precipitate the last portions. Ammonia may be employed instead of caustic soda, but then as small a quantity as possible of hydrochloric acid should be used, as calcium tartrate is somewhat soluble in ammonium chloride. The calcium tartrate is collected on a filter, washed, calcined—it need not be previously dried—and estimated volumetrically. An experiment made with 10 grams of pure cream of tartar gave 9·947. A mixture of cream of tartar, calcium sulphate, and calcium tartrate gave—

	Calculated.	Found. I.	Found. II.
Potassium bitartrate	92·3	92·5	91·8
Calcium tartrate (total)	128·2	128·5	127·5

An experiment made with a mixture of 10 grams of cream of tartar and 2 grams of calcium sulphate, proved the whole of the calcium to be precipitated as tartrate on addition of alkali to the acid solution.

R. C. W.

Adulteration of Volatile Oils. By LEONHARDI (*Arch. Pharm.* [3], xii, 490—493).—The author had occasion to test volatile oils bought at Trieste, Hamburgh, London, and Leipzig, as to their purity. He believes that the method employed by the German Pharmacopœia for testing the purity of these oils by mixing the sample with alcohol and then shaking it up with water in a graduated cylinder is very satisfactory, but in cases of expensive oils it is too costly. A simpler method is to pour a few drops of the oil under investigation over a few granules of red aniline (? rosaniline); if alcohol is the adulterant, a red coloration is obtained, if it is absent no change is observed. The following oils were examined:—

Stearoptene of Oil of Fennel.—This oil is at present imported largely from Russia, and is used for adulterating oil of anise, sometimes to the extent of 90 per cent. Like oil of anise, it has the property of solidifying at a low temperature. When warmed, the smell of oil of fennel is distinctly discernible.

Oil of coriander is largely used in the preparation of liqueurs. Owing to its high price it is often adulterated with colourless rectified oil of orange-peel. Pure oil of coriander is readily soluble in 90 per cent. alcohol, which is not the case if oil of orange-peel is present. Equal parts of this oil and 90 per cent. alcohol give a turbid solution.

Oil of bergamot is mixed with oil of orange; the ready solubility of the former, and the difficulty with which the latter dissolves in 90 per cent. alcohol, shows if it is adulterated.

Oil of cumin is often mixed with oil of cymene, the latter being again adulterated with oil of turpentine. The reaction with iodine, 90 per cent. spirit, and the smell, indicate the presence of these adulterations.

American oil of peppermint, as manufactured by Holtzsch, is said to be perfectly pure. It is sold in blue bottles, and to avoid adulteration a printed label is fixed over the stopper of the bottle. The author compared this oil with English or German oil of peppermint, and found that it was adulterated with oil of sassafras, various properties of the oil disagreeing with those of pure oil of peppermint; *e.g.*, turbidity was obtained with 90 per cent. spirit, dark red colour with sulphuric acid, the pure oil giving a brown colour.

In conclusion it is mentioned that for determining the purity of the above oils, Askinson's small book on *The Manufacture of Volatile Oils, &c.*, 1876, may be safely recommended.

D. B.

Some Reactions with Lindo's Test for some of the Bases in Opium. By HOW (*Chem. News,* xxxvii, 244).—The following reactions are obtained by Lindo's reaction with sulphuric acid and ferric chloride (*Chem. News*, xxxvii, 158, and this vol., p. 678):—

Papaverine dissolves in sulphuric acid to a pale purple fluid, which becomes very pale and then brownish on standing about an hour. The addition of ferric chloride and warming cause the purple colour to change quickly to yellow, while the liquid becomes turbid; the addition of water gives a colourless liquid, becoming pale yellow next day.

Narcotine dissolves to a bright yellow liquid, becoming orange on standing about an hour; then, treated as above, a blood-red is produced, soon assuming a purplish tinge, then a bright red, resembling ferric thiocyanate, and remaining permanent at least for a fortnight.

Cotarnine gives first a clear, dark brownish-yellow solution; then, with ferric chloride, a whitish precipitate, dissolving to a dark red liquid, which with water assumes much of the colour obtained with narcotine, but perhaps paler. It is equally permanent.

Narceine dissolves to an orange liquid, which becomes turbid and purplish, and finally of a pale red colour.

Strychnine dissolves to a colourless liquid, and affords successively a clear yellow and a colourless liquid.

Brucine gives first a pale amethystine solution, then orange-yellow or red-yellow looking across the tube, and red on looking down it; on further solution an amethystine-red, becoming pale, but still distinct, at the end of a fortnight.

Caffeine gives successively a colourless, a bright yellow, and a colourless fluid.

Piperine dissolves to a deep red, nearly black liquid, with a flocculent deposit on heating with ferric chloride; the addition of water gives a yellow liquid, the deposit appearing dark brown; the liquid was nearly colourless the next morning.

Betuline gives a dirty green-brown liquid, becoming clear and colourless with water.

Coumarin gives an orange-yellow clear liquid, which water renders very pale yellow.

Phloridzin (from bark of stem and roots of the apple tree) dissolves to a blood-red liquid, which is orange-coloured at first, if very little of the substance is used: water gives a small flocculent precipitate, and leaves the solution of an orange colour.

Quinine sulphate of commerce dissolves to a pale yellow liquid, which turns deeper yellow when warmed with ferric chloride, and colourless with water.

Cinchonine, impure, gives clear yellow, turbid yellow, and yellowish liquids.

Bebeerine sulphate, in brown scales, dissolves to a very dark liquid, becoming red with more sulphuric acid; with ferric chloride and warming, a dark green liquid—as seen over white paper—is produced, which gives with water a dirty yellow liquid. E. W. P.

Technical Chemistry.

Cleansing of Towns and Contamination of Rivers. By F. FISCHER (*Chem. Centr.*, 1878, 361—366).—Based on a resolution of the scientific deputation for medicinal purposes in Berlin, the German Government has ordered the authorities of Cologne and other towns to prevent human excrements from water-closets and other town refuse from being run into the sewers, and thence into the rivers. The author therefore made it his object to discuss this question more fully. With regard to the Rhine water, it is mentioned that although the water is still moderately pure, it is nevertheless being contaminated more and more every day, and since this water is used largely for drinking purposes, it becomes a very important and serious point to consider the future state of this river.

With regard to the other side of the question, namely, purification of the sewage (by irrigation), before it enters into the river, it is stated that such a process is not always suitable. The authorities of towns often raise much objection to this operation from a monetary point of view, and, besides this, it is not always possible to find suitable ground for such undertakings. The inhabitants will therefore be compelled, as heretofore, to collect all the refuse of their dwellings in underground reservoirs, thus contaminating the soil on which their houses are built, which the author considers to be worse than the contamination of the river. D. B.

Ozone-developer. By VULPIUS (*Arch. Pharm.* [3], xii, 534—536).—Gruner has patented the following apparatus, consisting of an ordinary Liebig's jar, which is used for preparing effervescing drinks: the jar is filled with an aqueous solution of acetic ether, a strong metallic tube being immersed through its top opening, while to the other end of the tube a metallic capsule is soldered, which is filled with a black brittle substance. A wick is passed through the tube, and the mass in the capsule is thus kept moist. The latter has a smell of turpentine, burns with a sooty flame on platinum, and proved to be a mixture of small pieces of resin with crude potassium permanganate, and a manganese oxide of a lower stage of oxidation—in fact a poor manganese ore which is of no use to the chlorine manufacture.

This apparatus does not evolve a trace of ozone, and is likely to mislead the public, as the materials have been chosen so that the mixed smell of resin and acetic ether may be similar to that of forest-air.

D. B.

Economical Value of Various Hydraulic Cements. By R. DYCKERHOFF (*Dingl. polyt. J.*, ccxxviii, 329—332).—In testing cements their tenacity is usually determined, whilst in practice it is their resistance to compression which is mainly employed. The relation between these varies with different samples. Experiments were made with Portland cement, Roman cement, and trass. Five samples of Portland cement, even when mixed with sand, gave a resistance to compression ten times the tenacity; whilst very good Roman cement (Grenoble) and trass (3 vols. best Beckum hydraulic lime, 4 vols. trass, 2 vols. sand, and also equal volumes of these) gave only six times. Hence a comparison of the tenacity of different kinds of cement is insufficient to determine their comparative value. Other properties than tenacity should be taken into account, such as the rate of setting, &c. The influence of this is clearly shown when the tenacity of a quickly setting cement is compared with that of the same cement after having been made to set more slowly by well known means. Thus a cement setting in 90 minutes had a tenacity of 7·6 kilos. per square centimeter after seven days, and of 13·8 kilos. after 28 days, whilst the same cement after being made to set in seven hours gave 10·9 and 15·9 kilos. respectively. The following table gives the tenacity of a cement setting in half an hour, and the same cement after being caused to set in 3½, 10, and 14 hours respectively.

Time of Setting.	Pure cement with 275 grams water to 100 grams cement.			1 part cement to 3 parts sand.		
	7 days.	28 days.	56 days.	7 days.	28 days.	56 days.
½ hour	22·7	28·5	37·7	8·1	11·8	15·7
3½ hours	22·2	32·1	37·5	10·0	14·9	17·9
10 "	26·4	35·7	42·0	11·2	16·7	19·2
14 "	29·9	38·2	44·9	12·7	18·5	20·2

Hence a good slowly setting cement has a higher tenacity than an equally good quickly setting one, so that this point is of considerable importance in testing a cement. J. T.

Glaze for Cooking Vessels with and without Lead. By L. Gallus (*Dingl. polyt. J.*, ccxxviii, 332—341; *Thonindustriezeitung*, 1877, 51—117).—The body of vessels which are to receive a lead glaze is made of a clay containing 20 to 40 per cent. sand; less than 20 per cent. of sand produces vessels which crack easily; with more than 40 per cent. the clay is difficult to work. If clay containing 10 to 20 per cent. sand be used, a dull red heat is not exceeded in burning ordinary stoneware, and a bright red heat for finer ware. Ground galena alone is often applied as glaze, with unsatisfactory results. A mixture of 1 part ground sand to 3 parts litharge, and sometimes with a little clay, is more generally used. For finer vessels a more refractory glaze is used, containing 2 parts litharge and 1 sand. These mixtures fuse to a smooth glaze on vessels whether rich or poor in sand, but cannot be employed with vessels containing much lime, as they are absorbed at a dull red heat, and produce a surface rough and dull. These glazes are volatile at a strong heat. All lead glazes of any thickness crack, so that injury to health may easily result from their use. A refractory, lustrous, durable, and cheap glaze free from lead is still wanting.

Bunzlau stoneware is glazed with a fusible loam, to which is added potash, soda, and borax solution. The body is made up of a refractory clay of the best quality, containing about 20 per cent. of sand, and to which about 20 per cent. more is added. Details of the best method of testing the fitness of the loam for glazing are given. J. T.

Behaviour of Phosphatic Pig-iron during the Puddling Process. By Kerpelg (*Chem. Centr.*, 1878, 352).—The following qualities of pig-iron were subjected to the puddling process:—

		Phosphorus.	Copper.	Sulphur.	Silicon.	Manganese.
Grey pig-iron,	No. 1	0·2484	0·033	0·085	1·420	0·010
„ „	No. 2	0·5200	0·106	0·082	2·020	0·040
„ „	No. 3	0·5970	0·130	0·041	1·006	0·046
White porous do.	No. 4	0·0450	0·099	0·171	1·374	0·061
Crystalline do.	No. 5	0·0500	0·043	0·113	1·499	2·758

Mixings were made in the double puddling furnace for granular pig and fibrous pig—

400 lbs. Nos. 4 and 5
300 „ No. 1
100 „ „ 3, and
100 „ „ 2

corresponding with 0·229 per cent. phosphorus.

Granular iron containing 0·0265, and fibrous iron with 0·0465 per cent. of phosphorus was obtained. In the first case 88·4, and in the second case 79·7 per cent. of the contents of phosphorus have been converted into slag, a circumstance which confirms Bell's results. A comparatively low temperature favours the removal of phosphorus during puddling, a difference of 9 per cent. in the granular iron produced having been obtained under the same circumstances, but at a lower temperature. D. B.

Copper Extraction at Oker in the Hartz. By Brauning (*Dingl. polyt. J.*, ccxxviii, 142—150).—The ores treated in the wet way at Oker, from the Rammelsberg mines, have, on an average, the composition given under (*a*); this corresponds mineralogically to (*b*).

(*a.*)

Cu	7·90
Pb	2·17
Ag	0·01
Fe	34·93
Zn	3·71
Mn	1·08
Co Ni	0·08
As Sb	0·08
SiO_2	1·70
Al_2O_3	2·61
$CaCO_3$	2·32
$MnCO_3$	0·74
$BaSO_4$	0·63
S	41·08
	99·04

(*b.*)

Iron pyrites	60	per cent.
Copper pyrites	23	,,
Blende	6	,,
Galena	2	,,
Gangue	9	,,

(*c.*)

CuO	9·80
Fe_2O_3	53·14
Pyrites	7·13
PbO	2·25
Ag	0·008
ZnO	2·43
Mn_3O_4	0·57
SO_3	9·51
Al_2O_3	4·43
Gangue	11·65
	100·918

As much as possible of the sulphur is burnt off for the manufacture of sulphuric acid, and the burnt ore has then approximately the above composition (*c*), as ascertained from a monthly examination.

The roasted ore is ground up with 15 per cent. of crude potassium chloride, and heated to dull redness with stirring. The active constituents of the potassium salt employed are the chlorine compounds of magnesium, potassium, calcium, and also the water. Undecomposed pyrites is oxidised: the sulphurous anhydride expelled is decomposed in presence of steam, alkaline chlorides, and possibly magnesium chloride in such a way that alkaline sulphates and hydrochloric acid are formed. The hydrochloric acid in *status nascendi* decomposes the oxides of copper, silver, zinc, manganese, and nickel, which are converted into chlorides, with simultaneous formation of water. The copper becomes partly cuprous and partly cupric chloride, and as these compounds are volatile at high temperatures, a dull red-heat should not be exceeded. Some copper pyrites remains unoxidised, and for the most part escapes conversion into chloride. For this process a suitable quantity of undecomposed pyrites should be left in the first roasting, or the addition of raw pyrites becomes necessary; also the mass of the copper should be present as oxide, and not as subsulphide. When the ordinary ore contains more than 8 per cent. of copper, too much subsulphide of copper results, and the metal is best extracted by smelting.

Analyses I and II show the composition of the mass at the middle and end of the roasting process. (20 per cent. of potassium salt was employed in this case.)

I.—Middle of the Process.

Soluble in Water.

Cu	1·94 per cent., as	$CuCl_2$	3·11
Ag	0·003 „	$AgCl$	0·004
Fe	0·74 „	$FeCl_2$	1·68
Al_2O_3	0·12 „	$Al_2O_3.3SO_3$	0·39
Mn	0·69 „	$MnCl_2$	1·58
Ni	0·20 „	$NiCl_2$	0·44
Zn	1·60 „	$ZnCl_2$	0·30
CaO	2·76 „	$CaCl_2$	6·27
MgO K_2O Na_2O	As sulphate from chlorine compounds		18·15
			31·924

Insoluble in Water.

Cu	4·32 per cent., as	CuO (sol. in HCl)	5·12
		Cu_2S (sol. in aqua regia)	0·29
Pb	0·39 „	$PbSO_4$	0·57
Fe	34·49 „	$Fe_2O_3.3SO_3$	3·27
		FeS_2	2·64
		Fe_2O_3	45·38
Al_2O_3	3·30 „	Al_2O_3	3·30
Mn	0·03 „	Mn_2O_3	0·04
Zn + Ni	0·29 „	ZnO + NiO	0·36
CaO	0·45 „	$CaSO_4$	1·09
SO_3	1·86		
S	1·47		
Cl	trace		
Insoluble in acids			2·96
			65·02

II.—End of the Process.

Soluble in Water.

Cu	3·86 per cent., as	$CuCl_2$	8·17
	0·005	$AgCl$	0·006
Fe	0·60	$FeCl_2$	1·38
Al_2O_3	0·17	$Al_2O_33SO_3$	0·56
Zn	0·64	$ZnCl_2$	3·42
Mn	0·75	$MnCl_2$	1·71
Ni	0·07 „	$NiCl_2$	0·15
CaO	1·60 „	$CaCl_2$	3·17
MgO K_2O Na_2O	as sulphate from chlorine compounds		20·05
			38·616

Insoluble in Water.

Cu	2·57 per cent., as	CuO	3·18
		Cu_2S	0·03
Pb	1·17 ,,	$PbSO_4$	1·26
Fe	34·56 ,,	Fe_2O_3	47·91
		$Fe_2O_3,3SO_3$	1·02
		FeS_2	1·18
Al_2O_3	0·44 ,,	Al_2O_3	0·44
Zn	0·37 ,,	ZnO	0·46
Mn + Ni	trace ,,	—	—
CaO	0·49 ,,	$CaSO_4$	1·19
SO_3	1·49		
Cl	trace		
S	0·64		
Insoluble in acids			3·69
			60·36

The solubility of the copper compounds is tested continually. On the average 75 per cent. of the copper in the ore is soluble in water, 20 per cent. in dilute acid, and 5 per cent. in aqua regia.

The ore is next extracted with a lye of somewhat variable composition; an idea of its composition may be obtained from Analysis III. 100 parts lye at 18° B. contain:—

Cu.	Pb.	FeO.	Fe_2O_3.	Al_2O_3.	ZnO.	MnO.	CO + NiO.	CaO.
0·015	trace	2·14	0·15	0·11	0·06	0·31	0·01	0·12

MgO.	Alkalis.	Cl.	SO_3.	SO + Sb.	Total acids.
0·52	2·61	2·56	5·89	trace	14 495

After standing at 50° for 4 to 5 hours, the lye is run off, and has the composition IV.

100 parts lye at 38° B. contain—

IV.		V.	
Cu	3·71	Cu	0·58 per cent
Pb	0·01	$Fe_2O_3 + Al_2O_3$	2·13 ,,
FeO	0·005	ZnO	0·06 ,,
Bi	trace	MnO	0·12 ,,
$Al_2O_3 + Fe_2O_3$	0·29	AO + NiO	0·02 ,,
ZnO	4·97	CaO	0·07 ,,
MnO	0·58	MgO	0·04 ,,
CoO + NiO	0·04	Alkalis	0·62 ,,
CuO	trace	Cl	0·13 ,,
MgO	0·27	SO_3	2·39 ,,
Alkalis	10·60		
Cl	12·56	Total solids	6·16
SO_3	8·95		
As + Sb	0·32		
[illegible] solids	42·305		

The ore is now treated with hot dilute hydrochloric acid, and subsequently with boiling sulphuric acid of 8° B. until the acid becomes general. The solution thus obtained has the composition V.

The copper is precipitated from these solutions by iron, and when dried at 100°, was found to contain 75·45 per cent. of pure copper, 6·72 of ferric oxide, 4·58 SO_3, besides traces of lead, zinc, &c.

The residue contains 0·3 to 0·8 of copper. Its analysis gave—

FeO_3	79 per cent.
Al_2O_3	3 "
MgO + alkalis	1 "
CaO	2·5 "
SO_3	5·5 "
Gangue, insoluble in acids	6 "
	97·0

100 parts of burnt ore give about 75 parts of residue. The small residue of copper is made useful in the Upper Harz works, where the residue is employed as flux. J. T.

Purification of Raw Lead and Elimination of the Silver. By Roswag and Geary (*Chem. Centr.*, 1878, 367).—This process is divided into the following operations:—(1.) The raw lead melted in a crucible is exposed to a pressure of 3—4 atmospheres, which is introduced into the metal bath by upright tubes, the mouth of which is placed about 4 to 5 inches above the bottom of the crucible. Almost all the impurities present in raw lead are oxidised, and form a frothy mass at the surface of the bath, which is taken off. This operation is continued until the lead assumes a violet-blue colour when cooled, and loses its brittleness. (2.) The partially purified lead is subjected to the ordinary desilvering process by means of zinc. (3.) The operation in (1) is then repeated, in order to remove the last impurities. (4.) The argentiferous zinc from (2) is treated with hydrochloric acid, until all the zinc has been dissolved. If any lead is present in the solution, it is thrown down by zinc, and is added to the undissolved residue of argentiferous lead. After being washed, it is melted in a crucible, and (5) the lead is oxidised to litharge by blowing in air. The litharge thus obtained contains all the precious metals. (6.) It is dissolved in pyroligneous acid, which leaves the silver as residue at the bottom of the vessel. After refining the silver, the operation is completed. D. B.

Formation of Naphthalene. By F. Tieftrunk (*Dingl. polyt. J.*, ccxxviii, 357—363).—Naphthalene is formed in two ways in the manufacture of coal-gas:—1. Tar, free from naphthalene, is produced, and this at a higher temperature yields naphthalene. 2. Olefiant gas is produced, and this at a red heat yields tar and naphthalene. Berthelot has also shown (*ibid.*, ccxxiv, 109, 226) that many of the products of coal distillation, styrene, and benzene, for instance, are built up from acetylene, and that naphthalene results from the combination of these with one and two molecules of acetylene respectively with separation of two atoms of hydrogen. The author defines tar to be all non-aqueous condensation-products of gas-making, which yield by fractional distillation phenol and its homologues. When phenol ceases to be found, these products become oily, and after this point begins the difficulty in gas-works of the deposition of naphthalene. The boiling points of phenol and naphthalene are not very wide apart, but their volatilities differ much, so that behind the scrubbers the phenol occurs, not as transparent vapour, but suspended in the gas in minute drops, and easily removed in the first purifier along with the naphthalene, which remains dissolved. If, however, a further condensation of the naphthalene vapour subsequently takes place, it separates in the solid state, the solvents phenol and tar-oil having been removed.

The condensation of those oils whose vapours exist in street-gas, and which hold naphthalene in solution, begins at temperatures from 0° downwards. For this reason the separation of naphthalene is more liable to take place from poor gas than from that of a better quality. To get an idea of the relation between these oils and naphthalene, air at 88° was passed through 1 liter each of tarry saw-dust from the first purifier, and also spent purifier charge kept at the same temperature; it was then passed through **U**-shaped tubes, kept at different temperatures, and finally through a glass worm, kept at − 21°, with the following results:—

Temperature.	I. First purifier.		II. Spent Purifier Charge.	
	Naphthalene.	Oil.	Naphthalene.	Oil.
	Per cent.	Per cent.	Per cent.	Per cent.
63°	—	—	—	—
50	0·8	—	—	—
38·5	2·2	—	1·3	—
25	2·3	—	4·1	—
12·5	—	1·6	0·9	—
0	—	1·8	0·3	—
−21	—	6·3	—	0·5
	5·3	9·7	6·6	0·5

Totals:—

Naphthalene	5·3	6·6
Oil	9·7	0·5
Water	85·0	92·9
	100·0	100·0

These numbers show that both masses contain naphthalene and oil, which were present in the crude gas. If street gas contained the vapours taken from the crude gas as indicated by I above, there would be little probability of a separation of solid naphthalene. But the relation between naphthalene and oily vapours is changed in the gas freed from sulphuretted hydrogen, as the figures above show. Not inconsiderable quantities of oil vapours are thus retained by filtration through saw-dust already impregnated with tar. From this and from the fact that large quantities of gas may be passed through a tube at 1° without depositing oil, it follows that gas between 25° and 70° is not saturated with oily vapour. Hence, if by lowering the temperature some naphthalene is separated, oil is not simultaneouslydeposited, and the separation of the former is at length arrested.

The constant presence of naphthalene in tar, a consideration of the great difference in the volatility of these bodies, and the fact that for naphthalene the time required for saturation with its vapour is very short, prove that crude gas is saturated with it. If, after passing through the oxide purifier, the gas is no longer saturated, a considerable lowering of temperature would be required to cause deposition of naphthalene. This occurs in late autumn, when along with high consumption, the purifiers are newly charged, and the charge is more porous, and therefore more absorbent than a spent charge. When the temperature has been lowered some degrees without deposition of naphthalene, a sudden appearance of cold weather causes decomposition of naphthalene in the neighbourhood of gas-works. J. T.

Chloroform containing Amyl-alcohol. By H. Werner (*Arch. Pharm.* [3], xii, 481—484).—When chloroform is used in medicine it is generally rectified, the German Pharmacopœia being satisfied with distilling commercial chloroform, prepared from alcohol, over a water-bath. The author has used the following treatment:—Chloroform is shaken up with one-fourth of its volume of distilled water. The latter is removed the next day, and the chloroform shaken up with fused sodium carbonate and allowed to stand for 24 hours. After removing the sodium carbonate, the residual product is distilled over a water-bath. For inhalation the distillate coming over below 64° is used, while the residue is used for external application. The first portions have the lowest specific gravity, and are turbid, the turbidity is, however, easily removed when the distillate is mixed with a small quantity of fused sodium carbonate (1—2 g.) The author has recently rectified about 5 kilos. of chloroform, and found in the residue small quantities of a substance resembling fusel oil in smell. In order to determine whether amyl alcohol was *really* present, the residue was distilled with sulphuric acid and potassium dichromate, when valeric acid was obtained. From chloroform rectified in the above manner, very satisfactory results were obtained, cases of vomiting being very few, which proved the absence of amyl alcohol. The origin of the latter in commercial chloroform is probably due to the fact that crude 80 per cent. alcohol is often used for the preparation of chloroform, and that during the rectification-process the vapours of chloroform carry over traces of fusel oil mechanically. In conclusion the author mentions that whilst chloroform boils over a naked flame at 62° to 63°, it does not boil below 64° when heated on a water-bath, and often not until a temperature of 66° has been reached. In the latter case it was difficult to determine whether the liquid was boiling, as the surface showed no signs of ebullition, a circumstance which is often observed with other volatile liquids, such as ether, benzene, &c. By immersing a piece of string in the chloroform to be distilled, the above difficulty was completely removed. D. B.

The Amount of Tartar in Wines. By M. BUCHNER (*Dingl. polyt. J.*, ccxxviii, 167—168).—The author first determined the solubility of tartar in dilute solutions of alcohol at different temperatures with the following results:—

Solution of alcohol per cent.	Tartar per cent. dissolved after 10 days.		
	At 0°.	At 6°.	At 15°.
7	0·15	0·225	0·260
8	0·13	0·206	0·220
9	0·11	0·187	0·206
10	0·10	0·162	0·187
20	0·075	0·092	0·112
30	0·037	0·056	0·056

It appears, therefore, that exposure to a low temperature may cause as much as half the tartar to be deposited, but time has considerable influence in this matter. The tartar so deposited does not readily dissolve again. The 10 per cent. alcohol solution at 15° gave 0·29 per cent. of tartar after 4 hours, whilst after 10 days it gave only 0·187.

In the following tables the tartar and ash do not altogether agree throughout the series:—

	Alcohol.		Extract.	Acid.	Tartar.	Ash.
	Wt. per cent.	Vol. per cent.				
WHITE WINES:						
Nussberger	8·98	11·11	1·74	0·62	0·17	0·12
Retzer	14·33	17·6	1·90	0·57	0·16	0·15
Mackersdorfer	7·50	9·3	1·69	0·66	0·18	0·17
Radiseller	9·34	11·57	1·81	0·68	0·19	0·13
Wind. Feistritzer	9·05	11·20	2·23	0·91	0·17	0·17
" "	8·27	10·20	2·21	0·89	0·15	0·16
Radkerburger, 1877	7·85	9·70	2·41	0·95	0·18	0·14
RED WINES:						
Bordeaux	8·91	11·04	2·23	0·64	0·15	0·20
Sexzarder	8·98	11·10	1·94	0·70	0·09	0·20
Fünfkirchner	8·91	11·00	2·09	0·70	0·12	0·14
Kalterer See	10·72	13·20	1·94	0·60	0·17	0·20
Istrianer	7·37	9·16	2·81	0·80	0·20	0·23
Dalmatiner	9·63	11·92	2·71	0·60	0·24	0·28

The author concludes that too low a temperature extracts a considerable part of the essential constituents, and must affect the taste of the wine; a low content of tartar does not prove the addition of water; moreover, the amount of tartar bears no definite relation to the amount of ash.

J. T.

Examination of Cinnamon and Pepper. By W. C. HERAEUS (*Arch. Pharm.* [3], xi, 440—443).—

	Ceylon cinnamon.	Chinese cinnamon.	Cassia lignea.	Cassia vera.	
Ash	2·4	6·2	2·2	4·0 to 7·0	per cent.
Soluble matter.	10·9	15·0	15·0	—	,,
Essential oil	1·4	9·0	2·2	—	,,

Some specimens of cinnamon contain from $\frac{1}{4}$ to $\frac{1}{2}$ per cent. of sugar.

	White pepper.	Black pepper.	
Ash	3·5	6·4	per cent.
Alcoholic extract	8·4	11·3	,,

M. M. P. M.

Quantitative Estimation of the Colour in Paper. By C. WURSTER (*Dingl. polyt. J.*, ccxxviii, 168—173).—The author proposes to ascertain the increase in weight of the ash due to the colour used. He has determined the increase in weight of the ash due to the colour alone in variously coloured papers with the following results:—

Colouring matter.			Weight of paper.	
Chrome-yellow ($PbCrO_4$)		Light-yellow paper	1·46	per cent.
,,	,,	Yellow paper	2·47	,,
,,	,,	Sulphur-yellow paper	4·52	,,
Chrome-orange	Pb_2CrO_5 and $PbCrO_4$	Light-orange paper	3·74	,,
,,	,,	Orange paper	6·75	,,
,,	,,	Dark-orange paper	16·00	,,
Red lead (reduced lead oxidised with nitric acid)		Light flesh colour	9·9	,,
		Orange-red paper	18·94	,,
Ochre		Dark-chamois-coloured paper	1·56	,,
,,		Light-chamois-coloured paper	0·79	,,

Earth colours.—These consist of clays coloured with various substances. The amount of colouring matter is very small. Thus two papers tinted with an ochre colour, but not so deeply tinted as the paper above mentioned, give an increase of 12·6 and 15·6 per cent. on the ash:—

Ultramarine	Light-blue post paper	0·36	per cent.
,,	Dark-blue post paper	1·50	,,
,,	Dark-blue post paper	1·70	,,
Prussian blue	Light-blue paper	0·97	,,
,,	Blue paper	1·44	,,
Pyrolusite	Grey paper	2·49	,,

Part of the MnO_2 will be converted into Mn_3O_4.

Brown coal and peat are also used to colour paper. Careful experiment will show that they have a perceptible effect upon the ash of the paper. J. T.

Aniline Black. By S. Grawitz (*Bull. Soc. Chim.* [2], xxix, 502—504).—By the action of an acid solution of aniline with metallic salts, or oxides of an oxidising nature, a black is obtained containing one or more atoms of hydrogen replaced by an equivalent of a metal. This black is not turned green by acids. L. T. O'S.

Use of Precipitated Sulphur in Dyeing Wool with Eosin. By M. Reimann (*Chem. Centr.*, 1878, 319).—Up to the present time dyers have always been under the impression that it is impossible to obtain bright colours with eosin on wool, unless the colour is fixed with precipitated sulphur as mordant. Instead of first boiling the wool in a bath of sodium thiosulphate and hydrochloric acid, as in the case of aniline-green, the colouring matter was at once added to the mordanting-bath with satisfactory results. The author experimented with precipitated sulphur prepared from sodium thiosulphate and hydrochloric acid, and found, by actual trials, that precipitated sulphur is without importance as a mordant for dyeing wool with eosin, the acting principle being the small excess of hydrochloric acid which liberates the acid from the potassium salt of tetrabromo-fluoresceïn—commercial eosin—and renders the colouring matter more suitable for being absorbed by the wool. It was further observed that acetic acid affords the most satisfactory method of dyeing with eosin on wool, the finest shades being obtained, whilst the operation is very simple and, when properly conducted, does not leave any pigment unused in the bath. D. B.

Use of Chromium Chlorate in Cotton Printing. By J. Despierres, W. Tatarinoff, and A. Scheurer (*Dingl. polyt. J.*, ccxxviii, 260—263).—This paper is a continuation of experiments which were described in *Dingl. polyt. J.* (ccxxv, 294). Chromium chlorate thickened with starch and printed on cotton, gives, after treatment with soluble glass, and dyeing in garancin, an undecided red colour, the shade of which may be compared with that of wine-lees. When "spirits of salammoniac" are used instead of soluble glass, the printed portions of the cotton assume a paler colour, whilst the whites are dirty. The basic chlorate under the same conditions yields darker shades. The temperature of the soluble glass bath must not exceed 40°. As a rule, better colours are obtained when the chlorate is used in the place of the nitrate or acetate of chromium. In the case of nitroalizarin, however, the nitrate gives a larger yield of the catechu colour than the chlorate.

The authors have prepared a new steam-black with chromium chlorate:—130 grams of wheat starch, 65 grams of torrefied starch, 0·5 litre of water, 100 grams of acetic acid, 400 grams of extract of logwood (sp. gr. 1·1598) are boiled, and 200 grams of basic chromium chlorate are added after cooling. This logwood black may be used alone for printing, or 3 parts of it may be mixed with 1 part of steam catechu, obtained by preparing a solution of catechu by dissolving

100 grams in 50 grams of water and 100 grams of acetic acid of 1·0506 sp. gr. 250 grams of this solution are boiled with 60 grams of wheat starch, 60 grams of burnt starch, 200 grams of water, and 200 grams of basic chromium chlorate are added on cooling. This steam catechu is steamed for one hour after printing, then washed and soaped for half an hour at 75°. Both blacks may be kept without altering. Scheurer mentions that by boiling the solution of chromium chlorate for some time very gently, much gas is evolved, which gives, when collected in soda-lye, a mixture of chloride, chlorate, and hypochlorite of sodium. By raising the temperature to 102 to 103°, a regular stream of oxygen is evolved, besides hydrochloric acid: 25 grams of liquid gave 675 c.c. of oxygen gas. The final residue consists of a crystallised mixture of potassium sulphate and chromic acid.

In conclusion Scheurer states that the action of chromium chlorate on indigo-blue and on Turkey-red dyed with artificial alizarin has also been studied. Dyed cotton was dipped into the solution at different temperatures until the colour was destroyed. The following observations were made:—

Indigo-blue.	Alizarin-red.	Temperature of liquid.
34 minutes	2 hours 23 minutes	50°
17 ,,	54 minutes	60
14 ,,	28 ,,	70
4 ,,	11 ,,	80
2 ,,	4 ,,	90

Note by the Abstractor.—The above statement of Scheurer respecting the evolution of oxygen on boiling a solution of chromium chlorate is very interesting; it would seem, however, that the author has omitted to state whether this takes place without the presence of sulphuric acid; in speaking of a solution of chromium chlorate, the author probably means the mixture of potassium chlorate and chrome-alum; this would explain the presence of the potassium sulphate and chromic acid found in the residue. D. B.

Preparation of Sulphuretted Oils having Insecticide Properties. By De la Loyère and Muntz (*Compt. rend*, lxxxvi, 1185—1187).—The authors have examined the oils produced by the distillation of the bituminous limestone found at Orbagnoux, near Seyssel, at the base of the Kimmeridge bed. The oils contain a large amount of sulphur in organic combination, to which they probably owe their fœtid odour and insecticide properties. The sulphur appears to be derived from sulphate of calcium, of which the mineral contains 1·2 per cent. By adding calcium sulphate or pyrites to the mineral before distillation, the quantity of sulphur in the distilled oils is increased, the calcium sulphate or pyrites being acted upon by the hydrocarbons with formation of volatile sulphur compounds. The amount of sulphur in the oils varies from 2 to 8 per cent., according to the substances added before distillation. The oils have a strong and persistent odour, and when warmed continue to disengage volatile sulphur compounds in great quantities for many hours. To destroy Phylloxera, a convenient plan is to use as absorbent the mineral from which the oil has been distilled, and which consists chiefly of calcium carbonate, containing a small quantity of sulphate, and traces of phosphates and of potash. The ammoniacal liquors containing the sulphur compounds which are produced during distillation are mixed with this, and the whole is applied as a powder to a depth of 3 or 4 inches around the vine stock. J. H. P.

Insecticidal Constituents in the Flowers of Pyrethrum corneum and P. roseum. By HAGER (*Chem. Centr.*, 1878, 368).—The peculiar action is due to two substances: the first a body related to trimethylamine, which is present in the flowers of the plant in combination with an acid. Large quantities could not be isolated; the action could therefore be tried only with flies. On moistening the mass with potash and holding a fly over it, the latter showed convulsive motions. The other more important and active part is the resinous dust from the petals, together with the prickly pollen. This dust seems to adhere with great tenacity to the body of insects, causing irritation. An aqueous and weak alcoholic extract of Persian insect powder is ineffective. The tincture of this powder also is not as active as the dry powder. D. B.

Preparation of Permanent Rennet-essence. By H. SOXHLET (*Dingl. polyt. J.*, ccxxviii, 341—349).—For the preparation of concentrated solutions, only dried calves' stomachs are suitable, and those which have been blown out with air and dried as quickly as possible are best. The small stomachs of the youngest animals are richest in ferment. Fresh stomachs are useless for preparing a concentrated essence, as they yield a thick jelly which, by filtering, gives only a small quantity of liquid. Concentrated extract prepared from stomachs after 14 days is light-yellow in colour, whilst that prepared after 6—8 months' storage of the stomachs is dark-brown. This results from slight decay of the stomach, and as the colour does not affect the usefulness of the product, it is advisable to use stomachs which have been stored for at least 3 months. The portion of the stomach without folds, the Portio pylorica, is cut away as it is poor in ferment.

Acid liquids are usually employed for extracting, as they seem to produce richer solutions, but this is only because they act more quickly at first than water alone. Hydrochloric acid containing 0·1 and 0·2 per cent. of acid in two days gave extracts twice as rich in ferment as an aqueous one; but after 8 days all three solutions were equally strong. A little thymol was added to prevent decomposition during the experiment. When the temperature is raised to 30—35°, water acts more rapidly than the acid, and the solution is richer than that produced by acid at the ordinary temperature.

Attempts were made to produce concentrated solutions by means of dilute acids, but without success. A 0·3 per cent. solution of salicylic acid gave a liquid which was quite fresh after 12 months, but after only 2 months its activity had fallen off to the extent of one-half.

A series of experiments made with solutions of common salt containing from 2 to 26 per cent. shows that solutions containing 3 to 6 per cent. of salt yield the liquids richest in ferment and capable of the highest degree of concentration. This property of dilute salt solutions depends on the fact made known by Graham, that common salt is a very easily diffusible substance. Organic acids in combination with common salt are no better extraction agents than the salt alone. 5 per cent. solutions of sodium or potassium sulphate are less efficacious than the same strength of salt solution. Potassium chlorate behaves in much the same manner as common salt; an excess of the chlorate, however, neither acts as efficiently as a precipitating agent, nor as a preventer of decomposition.

60 to 80 grams of calf's stomach steeped for five days in 1 liter of a 5 per cent. solution of common salt at ordinary temperatures, yield a solution of which 1 vol. will coagulate 10,000 vols. of new milk at a temperature of 35° in 40 minutes. If the filtered solution is treated with 60 to 90 grams more of stomach a solution of double strength is obtained; another repetition gives a solution three times the strength of the original one.

To prevent decomposition, about 0·3 per cent. of thymol may be added to the concentrated rennet extract solution. Possibly a slight taste due to this may be detected in the finest cheese, but for the same reason oil of cloves is much more objectionable. Boric acid is on all accounts the best antiseptic to employ, and solutions to which it has been added may be kept in covered vessels for months. All extract solutions lose strength on keeping; during the first two months the solution may become 30 per cent. weaker, then the strength remains nearly constant for eight months in the case of a solution of 1 : 18,000. Alcohol is almost as good an antiseptic as boric acid, if the solution be preserved in well-stoppered flasks.

Detailed experiments are given, showing that the time required to coagulate milk is inversely proportional to the strength of the extract solution. From this the strength of a solution can be determined by adding 1 c.c. to 1 liter of milk at 35°, and noting the time required to coagulate the milk; this time multiplied by 10 gives the time for the proportion 1 : 10,000. J. T.

Preparation of Black Leather Varnish and of Varnished Leather. By R. Hennig (*Chem. Centr.*, 1878, 317—319).—It is well known that varnished leather is prepared with the so-called "blue varnish" obtained by boiling Prussian blue with an easily drying oil. The preparation of this varnish forms the only secret of the whole manufacture. After drying, if of good quality, it should be flexible, elastic, and yet resistible, not sticky, fine black and shiny, and should not crack or strip off after exposure to the cold or after long wearing. It is difficult, however, to obtain a varnish with all these properties, success depending greatly on the manner of drying the leather after treatment, and on the knowledge of the reactions which take place during this operation, also of the fatty oils, their conversion- and decomposition-products. Linseed oil mostly forms the base of leather varnishes, a very clear and old oil free from water being used. The drying of all oil-varnishes is a process of oxidation, the oils being converted by the oxygen of the air into tough, transparent, and more or less caoutchouc-like bodies. To facilitate this oxidation, the oil is boiled with substances which readily give up oxygen. It is bleached if light varnishes are required. Palmitin, which is present in most drying oils, hinders the drying process considerably, and removes the fine lustre of the lacquer formed. This fat is removed by fuming nitric acid, palmitic acid and glycerin being formed, the former being subsequently separated as a lead or manganese salt. If the oil is not clear or not very old, and contains water, a previous treatment with concentrated sulphuric acid is necessary, or still better, to allow it to stand for 14 days with a concentrated solution of ferric sulphate with frequent stirring. The purified oil is then heated to 100°, and treated with a saturated solution of potassium permanganate (2 grams to 1 kilo. of oil). When the mixture assumes a brown colour, the temperature is raised to 130°, and boiling continued until all the water present has been expelled. Berlin blue is now added in the form of an extremely fine powder ($\frac{3}{4}$ to 1 kilo. to 10 kilos. oil). After 2 to 3 hours' heating, a portion of the mass is painted on writing paper. If on cooling a deep brown shiny layer is formed on the paper, the operation is finished. For specially fine lacquer, 10 kilos. of oil requires 300 grams of finely powdered gamboge. The latter is added after the completion of the above process, the mixture being heated to 150° for two hours. The temperature is then lowered slowly. Instead of grounding with lamp black and oil of turpentine, it is better to use an alcoholic solution of aniline blue, in which case the reddish-brown tinge always observed with the former mixture will not be noticed.

D. B.

Lignite-coke as a Substitute for Bone-Black. By F. MATTHEY (*Dingl. polyt. J.*, ccxxviii, 466—467).—Bone-black has for some time been replaced by another preparation obtained from the coke of lignite found in large quantities on the Continent. The coke is ground up in a mill, with water, to a very fine powder, and is, after drying, ready for use. Large quantities of this coke are at present manufactured, the conversion of coal into coke taking place in iron retorts, while the gases evolved are collected and used for fuel under the retorts.

D. B.

General and Physical Chemistry.

Universal Spectroscope. By Vogel (*Chem. Centr.*, 1878, 335).—Bunsen's spectroscopes, although well adapted for flame analysis, do not admit enough light, and are too cumbersome for investigating absorption spectra, a branch of spectroscopic work which is daily increasing in importance. The author recommends Browning's pocket spectroscopes, which are easily handled, and give a very bright spectrum. By means of a double reflecting apparatus, light is thrown sideways into the lower part of the slit, whilst the same light falls directly into the upper part. When an absorbing liquid is placed before the slit, the absorption spectrum is in the upper part of the field of vision, whilst the unaltered spectrum is seen in the lower: a comparison of the two allows of very accurate observation of the absorption phenomena, and, if daylight is used, the Fraunhofer lines enable their position to be determined. To facilitate the use of the instrument, the author has devised a light folding stand, which, besides the spectroscope, carries two clamps for holding test-tubes, which are preferable in his opinion, for the qualitative investigation of absorption spectra, to the more expensive absorption-boxes. When one liquid is placed before the slit, and another before the above-mentioned reflecting apparatus, the two can be very accurately compared. When liquids with very feeble absorption are to be examined, the spectroscope is placed vertically above them, and light is thrown up through the test-tube containing the liquid, by means of a mirror placed below; the stand also carries a clamp for holding glass.

When flames are examined they are placed before the slit, and a comparison flame before the reflector. The instrument may also be used for examining electric discharge spectra, and Geissler's tubes.

J. M. T.

Remarks on Vogel's Communication on "The Difference of Absorption Spectra of one and the same Body." By J. Moser (*Deut. Chem. Ges. Ber.*, xi, 1416—1417).—The author corrects what appears to have been a misunderstanding on the part of Vogel, of one of his previous works on this subject (*Pogg. Ann. Bd.*, 160, 177).

P. P. B.

Battery with a Single Liquid, Depolarised by the Action of Atmospheric Air. By Pulvermacher (*Compt. rend.*, lxxxvii, 22).—The exciting liquid (dilute sulphuric acid, or solution of potash, or of ammonium chloride) is placed in a cylindrical porous vessel; the positive metal is a rod of amalgamated zinc immersed in the liquid, and the negative metal is a slender wire of platinum or silver (according to the liquid employed) wound spirally round the porous cylinder. The coils of the wire are sufficiently separated from each other to avoid any capillary action; and at the number of points where the wire comes in contact with the liquid which exudes from the porous vessel, the oxidising action of the atmosphere continuously effects its depolarisation.

The electromotive force of an element charged with potash solution is 1·5 volt.; charged with dilute sulphuric acid, it is 1·16 volt. The resistance of a cell having a silver wire and a porous cylinder 35 millimeters in diameter, and 14 centimeters in height, was found to be 1·3 ohm. The electromotive force had fallen 16 per cent., when a circuit of 10 Ohms' resistance had been closed for ten minutes, and it recovered its initial value when the circuit was opened for three minutes. R. R.

Influence of Temperature on the Electric Conductivity of Liquids. By F. EXNER and G. GOLDSCHMIDT (*Wien. Akad. Ber.*, 1877, lxxvi, 455—475).—The object of the investigation is to ascertain the influence of temperature on the conductivity of liquids over as wide a range as possible, extending even beyond their normal boiling points. This paper contains results which have been obtained for water, both pure and acidified with sulphuric acid; no absolute determinations of resistance, however, have been made as yet, but only the relative determinations for the same liquid at various temperatures. In conducting the experiments, the temperature of the liquid was gradually raised from that of the room, the change in its resistance being meanwhile tested, and the liquid was then allowed to cool gradually, while the resistance was again observed at different points. In some cases curves are given exhibiting the results obtained.

In the first four series, the water was pure, and not raised above the boiling point. There was a considerable diminution in the resistance as the temperature rose, that at 20° being about three times that at 99°. This diminution was regular until the temperature reached about 75°, when it became more sudden. This arose no doubt from the water at that temperature attacking the glass of the vessel in which it was contained, as on cooling to the temperature of the room, the resistance was found to be permanently lowered.

In series 5—7 the resistance was observed at temperatures above the normal boiling point, the liquid being contained in closed glass tubes. The same general decrease in the resistance was observed, with the same sudden change about 75°. In series 8—11 a drop of 10 per cent. sulphuric acid was added to 30 c.c. of water. A minimum in the resistance was now observed about 80—90°, after which it rose again. In series 12 and 13 more acid was added, when the decrease in the resistance once more became regular as the temperature increased. The following appears to be the explanation of this anomalous behaviour of a weak solution of acid. The acidulated water attacks glass more readily than pure water, and sodium sulphate is formed. As there is very little acid present, the part neutralised to form sodium sulphate is a considerable part of the whole; but the addition of a very small quantity of acid will very much decrease the resistance, and conversely its removal will increase the resistance. The resistance of the water is therefore more increased by the combination of acid with the glass than it is decreased by the rise of temperature, and there is a minimum value of the resistance at the temperature where the glass begins to be attacked. When there is more acid present, that neutralised by the glass is so small a fraction of the whole that the conductivity of the liquid is not sensibly affected by the neutralisation. J. H. P.

Measurement of Heat at Various Depths in the Earth. (*Dingl. polyt. J.*, ccxxviii, 476).—In the Maria pit, near Aachen, the following determinations of the temperature at progressive depths were made during the construction of the shaft. The zero mark of the depths is 178·6 m. above the Amsterdam water-mark:—

Level.	Heat of the earth.	Temperature of the pit-air.	Daily temperature.
250 m.	15·2°	17°	13·2°
310	17·1	18	
370	19·15	17	
490	21·6	21	
562	24·2	26	

These observations were made with a differential thermometer. At each of the five levels a bore-hole 1 m. in depth, and filled with water, was made, which was closed perfectly air-tight before every observation. D. B.

Heat-conductivity of Cotton, Wool, and Silk. By J. Schuhmeister (*Wien. Akad. Ber.* 1877, lxxvi, 283—302).—Peclet concluded from his experiments, the first made with these substances, that the conductivity of cotton, wool, and silk was not very different from that of air, whilst Forbes subsequently found that cotton was a worse conductor when compressed than when divided, from which it would seem to be a worse conductor than air. These conclusions seemed to be so improbable, that the author investigated the subject afresh, using the same method as that by which Stefan determined the conductivity of gases, the substances being placed in the annular space between the air thermometer of Stefan's apparatus and the outer cylinder, which is the source of heat.

The results arrived at from a numerous series of experiments with atmospheres of both air and hydrogen are that both the gases are worse conductors than either cotton, wool, or silk, and that the greater the quantity of these substances between the cylinders, the greater is the conductivity. The following empirical formulæ were determined for the conductivity, K_m, of the substance, K_1 being that of the atmosphere employed, and p the weight of the substance in unit volume:—

Cotton........ $K_m = K_1 + 7·35\,p$
Wool .... $K_m = K_1 + 2·71\,p$
Silk.......... $K_m = K_1 + 2·50\,p$

These numbers are for the case where the fibres are in all directions. If they are arranged in some particular way, as for instance round the inner cylinder, the conductivity is different. The author also investigated the specific gravities of the substances, and found them to be—

For cotton .... $s = 1·707$
„ wool .... $s = 1·525$
„ silk .... $s = 1·498$

Using these numbers, he determined the conductivity, taking that of air as = 1, to be—

For cotton .... = 37
„ wool .... = 12
„ silk .... = 11

The cotton and wool employed were in the raw state, the latter being merino, whilst the silk consisted of cocoon fibres.

J. H. P.

Thermic Researches on Chromates. By MORGES (*Compt. rend.*, lxxxvii, 15—18).—The paper describes the thermic phenomena observed in the electrolysis of the chromates of potassium. The determinations of the amounts of heat concerned show that the electrolytic decomposition of the chromates is not comparable with that of the alkaline sulphates, and that, thermically, the chromates more resemble the carbonates.

R. R.

Thermo-chemical Study of some Phenol Derivatives. By W. LOUGUININE (*Compt. rend.*, lxxxvi, 1392—1394).—The present determinations were made in continuation of the author's researches to ascertain the influence, from the thermo-chemical point of view, produced by the replacement of hydrogen by electronegative elements or by electropositive or electronegative radicles.

The study of the sodium salts of the substituted phenols was rendered impossible owing to their instability during solution. The heat produced by the combination of Na_2O in solution with solutions of ortho- and para-mononitrophenol, of monochlorophenol (meta-, 215°), and of dichlorophenol (213—215°) respectively was ascertained: the numbers obtained were then compared with those given by Berthelot for phenol and picric acid. Dividing the difference between the heat of neutralisation of trinitrophenol and phenol by 3, the number + 2·13 is obtained; this corresponds with the introduction of the radicle NO_2. On adding this number to 7·4 (phenol), a number (9·53) is obtained fairly agreeing with ortho- (9·337) and not far removed from para-mononitrophenol (8·89). From this we may conclude that the heat of neutralisation of substituted phenols increases in proportion to the number of times that NO_2 is introduced. The results also prove that the introduction of NO_2 into phenol produces a much greater effect, with regard to the heat of combination with dissolved Na_2O, than the introduction of Cl. The group NO_2, once introduced, corresponds in this respect very nearly with 2Cl: the author has already obtained an analogous result by the thermo-chemical study of the substitution-products of aniline.

F. C.

On Vapour-densities. By L. TROOST (*Compt. rend.*, lxxxvi, 1394—1397).—The researches of Cahours on the variation in the vapour-densities of acetic acid and its homologues have proved that the vapours of these bodies, when near their boiling points, do not obey the laws of Mariotte and of Gay-Lussac. This fact has since been proved to be general, and applies to carbonic and sulphurous anhydrides, cyanogen, and other gases, when their densities are determined at low temperatures or under diminished pressures. Hence the correspondence between the density and the molecular weight holds good only under those conditions of pressure and temperature at which the body expands and contracts according to the same laws as hydrogen. Regnault has shown that the coefficient of expansion of carbonic anhydride corresponds with that of hydrogen, only at temperatures above 200°, or at pressures below that of the atmosphere. Following Regnault's method, the author shows that the vapour of acetic acid at a temperature of 130° and under the reduced pressure of 30·6 mm., yields a normal density of 2·10 (calculated, 2·09): also that nitrogen peroxide at 27° and 16 mm. pressure gives precisely the calculated vapour-density. Hence acetic acid and nitrogen peroxide behave like carbonic anhydride, and the application of the law appears to be general: it is, however, not necessarily applicable to all bodies. Soret has proved that the density of ozone is three-halves that of oxygen, and that this result is *independent of the pressure* and of the temperature within certain limits. Bearing this in mind, we can determine by experiment whether sulphur vapour is analogous to ozone or to carbon dioxide: its density decreases gradually from 6·6 (three times its theoretical density) at 440° to 2·2 (the theoretical number) at 860°. If the vapour-density at 440° decreases under diminished pressure, sulphur vapour is analogous to carbon dioxide; if the density remains unaltered, sulphur vapour at 440° is like ozone. Sulphur vapour at 440° and under 104 mm. pressure gave 6·7 density, and under 60 mm. it gave 6·3: hence sulphur vapour at 440° is a body analogous to ozone, its density remaining unaltered under diminished pressure, but gradually decreasing with elevation of temperature.

The author has experimentally confirmed his previous results as to the physical condition of the vapour of chloral hydrate at 78°, and as to the tension of dissociation of neutral potassium oxalate at the same temperature.

F. C.

Inorganic Chemistry.

Action of Iodine Trichloride on Carbon Bisulphide. By J. B. HANNAY (*Chem. News*, xxxvii, 224).—The author has quantitatively examined Weber's statement that a new product is formed when iodine trichloride is added to carbon bisulphide, and has obtained results which show the reaction to take place according to the equation—

$$2CS_2 + 3ICl_3 = CCl_4 + CSCl_2 + 3SCl + 3I.$$

A. J. C.

On Nitrogen Trioxide prepared from Starch and Nitric Acid, and on the Nitrogen Trioxide of the Sulphuric Acid Chambers. By G. LUNGE (*Deut. Chem. Ges. Ber.*, xi, 1229).—On gradually adding nitric acid (sp. gr. 1·33 at 20°) to a thick emulsion of starch heated on the water-bath, pure nitrogen trioxide is evolved, and may be dissolved in sulphuric acid, forming nitro-sulphonic acid $SO_2(OH)(NO_2)$.

Lead nitrate when heated yields only nitrogen tetroxide. The experiments were conducted so as to determine the amount of nitrogen tetroxide given off by starch and nitric acid, if such were the case. In sulphuric acid chambers it is argued that NO_2 is not present, except perhaps in the last chamber where there is a deficiency of sulphuric acid, because the nitrogen tetroxide is converted into the trioxide and nitric acid by the action of sulphuric acid. E. W. P.

Solubility of Phosphorus in Acetic Acid. By G. VULPIUS Arch. Pharm. [3], xiii, 38).—Phosphorus when heated with concentrated acetic acid is dissolved to the amount of 1 per cent.; this solution is rendered turbid when slightly diluted, by reason of the separation of phosphorus, the liquid at the same time becoming highly phosphorescent. In this state the phosphorus is rapidly oxidised, whereas the clear solution oxidises but slowly, if at all.

E. W. P.

Decomposition of Ultramarine by Carbonic Acid. By S. SUGUIRA (*Chem. News*, xxxvii, 213).—Ultramarine is decomposed, with evolution of hydrogen sulphide, by an aqueous solution of carbon dioxide, and therefore cannot be employed as a safe indicator of free hydrochloric acid in the presence of carbonic acid, as proposed by H. Müller (*Chem. Soc. J.*, xxiii, 38). A. J. C.

Ultramarine. By KNAPP and P. EBELL (*Dingl. polyt. J.*, ccxxix, 69—80 and 173—178).—The first part of this paper refers principally to blue ultramarine as compared with green or red ultramarine, the object in view being to explain the formation of the blue colour, to investigate the conditions of its development, and to determine its nature.

The preparation of ultramarine is always divided into two operations: formation of the raw product, and conversion of the latter into the blue colour.

I. Condition of the Formation of the Crude Fused Product.—By starting with Gentele's mixture—mostly used for the preparation of ultramarine—viz.:—100 parts of kaolin, 100 parts of soda, 60 parts of sulphur, and 12 parts of coal, and fusing the whole for five hours in a furnace charged with coke at a bright-red heat, we obtain a product resembling the crude ultramarine of works in appearance and consistency.

The first question which naturally presents itself is, what change with regard to the proportional weights of these different substances can be made, and how does this alteration influence the development of the blue colour? With regard to a change in the quantity of kaolin it was shown that the property which the fused product possesses of giving a blue colour is limited by the ready fusibility of the mixture. The latter is observed to occur when a decrease in kaolin has taken place. Soda gave a different result: by decreasing its quantity from 100 pts. to 50 pts., the mass obtained had an appearance similar to that of the above-named raw ultramarine, the difference being that it did not lose large quantities of sodium sulphide in water, but nevertheless evolved hydrogen sulphide with acids. 25 parts of soda formed a white product which neither gave a blue colour nor formed hydrogen sulphide with acids. An increase in the quantity of silicic acid seemed to produce no material change in the formation of raw ultramarine. A considerable excess, however, gave unsatisfactory results (120 parts were added), the formation of sodium sulphide being rendered impossible by the fact that the large excess of silicic acid absorbs the total sodium present. Mixtures without the addition of silicic acid are difficult to work, the fused mass being frequently converted into a slag. The loose, uncompact, porous nature of the fused product forms an indispensable condition for the development of the blue colour.

In order to obtain a more accurate insight into the important part which kaolin takes in the formation of crude ultramarine, the former was replaced by its main constituents: silicic acid in the form of quartz, and alumina. The following proportions were used:—45 pts. quartz, 37 pts. alumina, 100 pts. sodium carbonate, 60 pts. sulphur, and 12 pts. coal. The results were unsatisfactory, inasmuch as in the fusion process the quartz only had been rendered soluble, combining with the total contents of sodium present, leaving the alumina unused in the reaction. In another trial the quartz was added in the second part of the fusion operation; in this case favourable results were obtained. These observations seem to show, that for the successful development of a fine blue colour, it is indispensably necessary to render both constituents—silicic acid and alumina—simultaneously active in the fusion process. As to the presence of sulphur in the ultramarine mixture, it was scarcely necessary to try experiments, since the effect of an increased or decreased addition is too well known. A decreased quantity gave a fused mass having a large fusing power, whilst a reduction to 7·5 parts gave a perfectly useless product. Besides the ready fusibility of the mass, the failure of the latter is due to the fact that the amount of sodium sulphide formed is not sufficient. An excess of sulphur acts as a reducing agent; in this case the addition of coal is unnecessary.

The authors now proceed to give a detailed account of their investigations regarding the appearances observable during the fusion, and the manner in which the various ingredients act on one another. It is stated that the temperature required for the formation of the crude mass must be such as to avoid not merely the melting of the latter, but also fritting. In the fused state silicic acid is neither changed by sulphur nor by sodium thiosulphate. By treating quartz meal (obtained from a porcelain manufacture) with sodium sulphide at a red heat no change was observed. This tends to show that silicon sulphide is not formed in the crude product; the formation of aluminium sulphide, however, has been supposed to take place. The latter is easily obtained by introducing sulphur into melted metallic aluminium. The compound formed—not black, but of light yellowish-grey colour—evolves hydrogen sulphide under water, alumina being separated as flakes in the water. The question whether aluminium sulphide is produced in a similar manner from alumina and not from the metal in the formation of ultramarine, is answered negatively, although Frémy and Vincent have succeeded in obtaining aluminium sulphide by the action of carbon bisulphide vapours on red-hot alumina.

In conclusion of the first part of the authors' paper it is mentioned that sodium thiosulphate behaves in the same manner as a mixture of free sulphur and soda. Sodium sulphate reduced by coal at a red heat gives ultramarine. The question whether free sulphur forms a decomposition-product of ultramarine with acids, or is present in crude ultramarine, or in blue ultramarine, cannot be decided by analysis, so long as the oxygen is determined by difference. Further proofs will show that it is possible to have a quantity of free sulphur in these products, in spite of the volatility of this element at a red heat.

II. *Conversion of Crude into Blue Ultramarine.*—On continuing the roasting operations for some time, with access of air, crude ultramarine assumes a blue colour, in the presence of an excess of sulphur. Although the development of the blue colour has always been attributed to the action of the sulphurous acid produced, it is found that the latter is not the only active agent in the formation of the blue. When sulphur is burnt, sulphuric anhydride is formed in small quantity, as well as sulphurous acid, and acts like sulphurous acid on the crude ultramarine, as may be shown by passing the vapours of sulphuric anhydride over it. The best and most suitable means of blueing crude ultramarine on the small scale is dry hydrochloric acid gas. Ammonium chloride possesses the same property, as at high temperatures it becomes dissociated into a mixture of hydrochloric acid and ammonia vapour. Carbon disulphide, carbon dioxide, anhydrous phosphoric acid, and anhydrous boric acid, have also the same blueing property. Chlorine is very powerful. In all cases heat is required to effect the conversion. Neither heat nor air alone is sufficient for the formation of the blue colour.

From the results of the authors' observations, the following would appear to be the conditions for the formation of crude ultramarine, and its conversion into ultramarine blue:—

(1.) Fixed and invariable proportions of the weights of the mixed substances (forming crude ultramarine) are unnecessary, considerable latitude being allowable in this respect.

(2.) It is indispensable that the combination of the alumina and silica should be broken up by the heating process.

(3.) Soda must be added in quantity sufficient to produce an abundance of sodium sulphide as well as silicate.

(4.) Crude ultramarine must be capable of evolving large quantities of hydrogen sulphide.

(5.) The oxygen-compounds of the sulphur are not integral ingredients of either crude or blue ultramarine.

(6.) The formation of aluminium sulphide does not take place during the ignition.

(7.) The ingredients forming the mixture must be as finely divided and mixed as intimately as possible, in order to form a homogeneous product and a uniform blue.

(8.) The temperature to which the mixture is heated must be sufficient to completely displace the alumina, and to form sodium sulphide, but it must never be so high as to cause fritting or actual fusion of the mixture.

(9.) For the production of crude ultramarine, one hour's heating is needed, as the reaction takes place gradually.

(10.) The conversion of ultramarine into the blue is effected by the action of anhydrous acids (chlorine) at a moderate red heat, and is always accompanied by the separation of free sulphur, and the formation of a corresponding sodium salt. D. B.

Gallium. By L. DE BOISBAUDRAN and E. JUNGFLEISCH (*J. Pharm. Chim.* [4], xxvii, 338—340; see also this Journal, p. 556).—Crystals of gallium are obtained by introducing into the metal, cooled 10—15° below its melting point, a piece of platinum with a particle of solid gallium attached to it. In from 3 to 10 seconds octahedrons form, which are modified at the summit by traces of the basal face. If these crystals are not directly removed, the metal becomes heated nearly to its melting point, solidification is retarded, and the basal face is so much developed that large tables are formed. The reason for this variable development of the faces of the same crystal has already been given by the author.

The crystals of gallium are very brilliant, but are difficult to measure owing to their faces being slightly rounded. The authors hope to overcome this by preparing the crystals by slow electrolysis.

Thin wire may be bent several times without breaking, but a rapid flexion or shock fractures it at once, in the same direction as the cleavage of the crystals.

Thin plates were prepared by fusing the metal between hot glass, when, after cooling, the sheet was easily removed under water. Crystals of gallium prepared in the cold by electrolysis from a potash solution, decrepitate when placed in cold water, at the same time giving off bubbles of gas. But when the liquid is heated above 30°, and submitted to electrolysis, very frequently towards the end of the operation a pasty metal is formed which swells up in tepid water, and has the appearance of ammonium amalgam; when well mixed with water at 40°, it contracts, and becomes converted into ordinary liquid gallium.

The authors believe that gallium is frequently alloyed with small quantities of an alkali-metal. When it is deposited by electrolysis, a trace of zinc comes down with the gallium, from which the latter can be almost entirely freed by prolonged agitation with tepid water acidulated with hydrochloric acid. The oxide of the metal is soluble in ammonia. Bromine has a less energetic action on the metal than chlorine, nevertheless it combines with it in the cold, with evolution of heat. The bromide is white, crystalline, and deliquescent, but less volatile than the chloride. The iodide may be obtained by gently heating the materials together; it is crystalline, but not colourless, probably owing to free iodine which it retains; it is fusible and volatile, but less so than the bromide, undergoing partial decomposition when strongly heated. It is deliquescent. R. C. W.

Zinc-dust. By F. A. THUM (*Dingl. polyt. J.*, ccxxix, 56—57).—With reference to Lencauches's experiments described, *ibid.*, ccxxviii, 267, the author mentions that 1 litre of zinc-dust weighs, in a loose (unpressed) state, according to the degree of purity, 2·5 to 3 kilos., the sp. gr. varying from 6 to 7. This fact shows that the former chemist's statement regarding the sp. gr. of zinc-dust is not correct, it being mentioned that this powder is scarcely as heavy as water. It is not practicable to work up zinc ores exclusively for the production of zinc-dust, the loss being too great.

With regard to the tension of zinc vapour, which Lencauches supposes to be not higher than the atmospheric pressure, even at the highest temperatures, the author has but little doubt, that in the present state of science it would not be possible to disregard Mariotte's in this case any more than any other law. D. B.

Action of Water and of Saline Solutions on Zinc. By SNYDERS (*Dingl. polyt. J.*, ccxxviii, 477, from *Deut. Chem. Ges. Ber.*, xi, 936).—The solubility of zinc in well-water depends on the proportion which exists between the carbonates and phosphates, and the chlorides, sulphates, and nitrates. The most injurious salts of the latter class are the ammonium salts, then the chlorides of the alkaline earths, and the chlorides and sulphates of the alkalis. Hard well-water does not act on zinc. Soft water and rain water containing ammonium salts act on this metal. D. B.

Double Compounds of Metallic Sesquisulphates. By A. ETARD (*Compt. rend.*, lxxxvi, 1399—1402).—The persulphates can yield salts of the general formula $M_2(SO_4)_3.N_2(SO_4)_3$, and these can further combine with a molecule of sulphuric acid. The author has prepared salts in which M and N in the above formula are represented respectively by iron and aluminium, iron and chromium, aluminium and chromium, manganese and iron, and chromium and manganese.

$Al_2(SO_4)_6Fe_2.SO_4H_2$, is obtained in microscopic hexagonal plates by heating to 200° a concentrated solution of 2 molecules of ferrous sulphate, and 1 molecule of aluminium chloride which has been mixed with nitric acid and a large excess of strong sulphuric acid; the sandy deposit was separated by decantation, washed with glacial acetic acid, and dried at 120°. When heated to dull redness, this salt loses sulphuric acid, and $Al_2(SO_4)_6Fe_2$ is left as a white crystalline insoluble powder.

The method of preparation of the double salts containing chromium was similar, chromic acid being used.

The double salts containing manganese were prepared by heating a solution of manganous sulphate and of the other compound in the requisite proportions to 250°, and adding a mixture in equal volumes of sulphuric and nitric acids in small quantities at a time. When warmed with hydrochloric acid, the compounds containing manganic sulphate evolve chlorine. The double sulphate of aluminium and manganese contains two molecules of aluminium sulphate to one of manganic sulphate. F. C.

Analysis of Iron Ores. By LIPPS and SCHNEIDER (*Dingl. polyt. J.*, ccxxviii, 474, from *Berg-und hüttenmännisches Jahrb.*, 1878, 200).—The authors have examined spathic ironstone from Gollrad, with the following results: I. Roasted and lixiviated. II. Roasted with coal-waste from Löben, not lixiviated. III. Roasted with charcoal-dust, not lixiviated.

	Fe_2O_3.	FeO.	Mn_3O_4.	CuO.	CoO.	Al_2O_3.	CaO.
I.	67·61	2·60	3·35	0·030	traces	0·94	1·15
II.	62·64	2·00	3·33	0·013	,,	3·55	1·25
III.	64·30	1·89	3·05	0·006	,,	1·76	1·30

	MgO.	Quartz and combined SiO_2.	H_2SO_4.	H_3PO_4.	CO_2 and H_2O.	
I.	8·41	13·80	0·31	0·04	1·45	= 99·690
II.	10·35	13·15	2·46	0·02	1·80	= 100·563
III.	8·62	15·48	2·23	0·04	2·00	= 100·676

D. B.

Properties of Iron-Alloys. By G. H. BILLINGS (*Dingl. polyt. J.*, ccxxviii, 427—431).—These experiments were undertaken (*Engineer and Mining Journal*, 1878, xxiii) with the view of determining the influence which the absorption of other metals exercises on the properties of iron. The author experimented in one case with pure iron poor in carbon, and repeated his experiments with iron containing gradually increased quantities of carbon. In each case 7 kilos. of iron were worked up in an open crucible, exposed to the flame of a Siemens-Martin regenerative furnace.

Iron and nickel gave a perfect alloy, behaving like iron at a white heat. The composition of the alloy was 0·732 p.c. nickel, 0·07 carbon, and the sp. gr. 7·787. When the carbon is increased, the action of nickel is weakened. By rolling the alloy made with a large proportion of carbon into bars, and welding, they are rendered red-short after hammering.

Iron and copper (2 p. c.) give red-short castings, with dark grey granular fracture. When turned, polished, and etched, they showed homogeneity without distinct crystalline structure.

Iron and tin form a brittle alloy with fine crystalline structure. The alloy appears homogeneous when turned and polished. Its composition was 0·73 p. c. tin, 0·06 p. c. carbon, and the sp. gr. 7·805. Tin proved to be the most injurious to iron of all metals used in these experiments.

Iron and platinum combine at a comparatively low temperature, and in any proportions. Unless equal quantities of carbon are present, the alloy cannot be worked at high temperatures. The alloy breaks when rolled if a small quantity of carbon is present.

Iron and antimony give an alloy with blistered and coarse crystalline fracture, not resisting welding or hammering, being both cold and red-short.

Iron and bismuth give an alloy harder than pure iron, with fracture resembling that of Bessemer steel; does not resist welding or rolling.

Iron and molybdenum combine very readily, forming an alloy perfectly useless for any purpose.

Iron and zinc form an alloy which cannot be rolled or welded without breaking. Mere traces of zinc influence the quality of iron very considerably.

Iron and lead. The same as the former.

Iron and silver combine with difficulty.

Iron and cobalt form an alloy weaker than iron, and not resisting rolling into bars. D. B.

The Allotropic Condition of Metals. By P. SCHUTZENBERGER (*Compt. rend.*, lxxxvi, 1397—1399).—After referring to previous experiments of his own and of Gore, which furnished copper and antimony apparently in an allotropic condition by electrolysis, the author describes recent experiments by which he obtained lead in a remarkably oxidisable condition: he considers that these examples might be multiplied by subjecting different metallic solutions to electrolysis under suitable conditions.

The current from a Bunsen element is passed through a ten per cent. potash solution, the positive electrode being a sheet of lead and the negative a sheet of copper or polished gold: the electrodes are placed parallel, and three or four centimeters apart. As soon as a little lead has been dissolved, a bright bluish-white metallic film is deposited on the negative plate.

If the negative plate is at once removed from the bath and exposed to the air, after having been washed with tepid water which has been boiled, the film rapidly vanishes, causing the yellow colour of the subjacent metal to appear. After drying, it becomes evident that in reality a film of yellow lead oxide has been formed, which while moist did not conceal the metal beneath.

Hydrogen is constantly liberated from the negative plate during the electrolysis, and consequently the amount of lead dissolved from the lead plate is greater than that deposited on the negative electrode. As soon as the quantity of lead in solution ceases to be very small, the deposit instead of being smooth, appears as a bulky grey sponge, together with very delicate hairs or feathers. This sponge after having been washed with boiled water and dried in a vacuum, yields a metallic powder which on exposure to air is changed in less than an hour into a crystalline talc-like oxide.

As soon as the vertical distance between the electrodes becomes much reduced by the growth of this sponge, or when the bath is too highly charged with lead, the deposit suddenly changes to brilliant plates (arbor Saturin).

Allotropic copper, obtained by electrolysis of the acetate, always contains a little acetate and oxide, hence it is impossible to decide whether it contains any occluded hydrogen; but since this hydrogen would not exceed 0·03 per cent., it is difficult to conceive any alteration of properties resulting from its presence in quantity so small. The following experiments prove that the differences observed result from allotropic modification. A fresh sheet, which liberated only a mixture of nitrogen protoxide and nitrogen from 10 per cent. nitric acid, was heated in a sealed tube for 24 hours at 100°, with water slightly acidified with acetic acid: after cooling, there was *no increase of pressure*, and the copper when treated with weak nitric acid yielded nitrogen dioxide

mixed with 10 per cent. or more of protoxide. When heated with water alone, the change is produced, but more slowly or less perfectly: it would appear that the higher the temperature employed, the lower is the proportion of nitrogen protoxide subsequently yielded on treatment with dilute nitric acid. It is probable that for each condition an equilibrium is established between the two varieties of copper.

Cuprous oxide in fine powder when treated with cold 10 per cent. nitric acid behaves like a mixture of copper and cupric oxide: cupric nitrate is formed in solution without any evolution of gas, and finely divided copper remains in a condition not attacked by dilute nitric acid at ordinary temperatures, and possessing therefore properties directly the converse of the electrolytic copper referred to above.

F. C.

Bismuth Subnitrate. By A. Riche (*Compt. rend.*, lxxxvi, 1502—1505).—An examination of a number of specimens of bismuth subnitrate from different manufacturers showed that they all contained lead in sufficient quantity to give a precipitate with dilute sulphuric acid; but a further examination of the white precipitate proved that it was very complex and by no means wholly composed of lead sulphate. The weight of total precipitate obtained varied from 0·58 to 0·16 per cent., but while the former contained 0·334 per cent. of lead instead of 0·396, the latter contained only 0·033 per cent. instead of the theoretical quantity, 0·109. One specimen which contained no lead whatever, gave 0·18 per cent. of precipitate containing theoretically 0·123 per cent. of metallic lead.

The quantity of lead actually present in any sample did not amount at the most to more than $\frac{1}{1000}$th part; a proportion which must be considered too small to be dangerous.

By precipitating a solution of bismuth containing 2 per cent. of lead, with pure distilled water, according to the directions of the Codex, a subnitrate was obtained which did not contain a trace of lead; but on adding ammonia to the filtrate so as to leave the solution slightly acid, a further precipitate was obtained, containing nearly one-half per cent. of lead. Again, by substituting well-water containing calcium carbonate and sulphate for distilled water, the precipitated subnitrate gave, on solution and addition of dilute sulphuric acid, 0·775 per cent. of crude sulphate, containing 0·056 per cent. of lead instead of the theoretical amount, 0·529 per cent.

The formula $BiO,NO_5 + 2Aq$ requires 17·64 per cent. of nitric anhydride, but several specimens of subnitrate precipitated by distilled water contained only 14 to 15 per cent., while that precipitated by the partial addition of ammonia contained about 9·0 per cent. The subnitrates of commerce were found never to contain more than 12·0 per cent.; one sample even falling as low as 0·898 per cent.

From these experiments the following conclusions may be drawn—

1. That it is possible to produce pure subnitrate from bismuth containing lead, by the addition of distilled water only.
2. That the subsequent partial addition of ammonia should be avoided.
3. That well-water should never be substituted for distilled water.

J. W.

Occurrence and Working of Mercury Ores. (*Dingl. polyt. J.*, ccxxix, 168—173).—The principle of the preparation of mercury from its ores is very simple. It suffices to ignite the ores in closed vessels with lime for the removal of the sulphur, and to condense the vapours formed, or to undertake the desulphuration by merely introducing air, whereby the sulphur is burnt to sulphurous anhydride, the latter passing into the atmosphere. The main difficulty is the condensation of the mercury vapours, an operation which has not yet been effected without great loss, although many improvements have been made in this direction.

The chief districts for the production of mercury are: Almaden in Spain, Santa-Clara in California, Idria in Austria, and formerly Zweibrücken in Bavaria. According to the most recent accounts mercury ores have been found in quantity in Borneo. In Bavaria the ores were distilled with lime in retorts with clay receivers containing a small quantity of water. Ure afterwards improved on this plan by using cast-iron retorts fitted with a tube from which the vapours were passed into a condenser. For the desulphuration by burning with access of air, an apparatus is recommended, consisting of large brick chambers in which ore and fuel are piled up in alternate layers, whilst air is introduced through openings at the bottom. The mercury gradually collects in the upper part of the mass, and when this is rich enough it is washed to obtain the metal. The loss is about 12 per cent., but in numerous other forms of apparatus constructed on a somewhat similar principle the loss is far greater. At St. Clara, California, an improved form of condenser has been tried. The apparatus consists of a large chamber, in which the greater part of the flue-dust is deposited, and of three smaller chambers connected with the larger one, and communicating with one another at the top and bottom alternately. These chambers subsequently open into a series of smaller chambers in connection with the main shaft.

In 1870 Pellet constructed an apparatus in which the vapours pass through a long system of chambers, where they are thrown down with artificial rain fall. This method seems to give the most satisfactory results, the condensation being so complete, that the escaping vapours do not contain even a trace of mercury.

In conclusion, an account is given of the principal localities at which mercury mines exist. It is shown that North America produces one half of the total quantity of mercury brought into commerce, Spain and Austria being the next largest producers. The quantity of mercury produced in 1876 in the whole world amounted to a total of 126,600 bottles, containing 34·7 kilos. per bottle, of which North America produced 69,200 bottles, Spain 41,700, and Idria 8,000 bottles.

D. B.

Mineralogical Chemistry.

Structure of certain Minerals. By GAUDIN (*Compt. rend.*, lxxxvii, 66).—In this paper the author deduces the molecular constitution of certain minerals from peculiar theories as to their crystalline structure. Thus, the crystallisation of lead and calcium tungstates and molybdates he considers to prove that tungstic and molybdic acids are analogous to alumina, to boric acid and to arsenious acid, and not to sulphuric or chromic acid. The emerald he regards as composed of 27 molecules of silica, 4 of alumina, and 10 of glucina, arranged so as to form 7 regular hexagons. R. R.

Occurrence of Marsh-gas in Old Coal Pit Workings. By J. COQUILLION (*Compt. rend.*, lxxxvi, 1320—1322).—From several observations and determinations of marsh-gas in old coal pit workings, the author concludes that marsh gas does not occur diffused through the atmosphere of these workings, but has a tendency to accumulate in layers, and otherwise localise itself. Several of these determinations were made by means of a portable apparatus invented by the author and styled a "grisoumètre portatif." P. P. B.

Analysis of the Spring Water of Marpingen. By H. VOHL (*Deut. Chem. Ges. Ber.*, xi, 878).—The analysis of this water gave the following constituents in 1 litre:—

Milligrams.								Organic and volatile
CaO.	MgO.	Fe_2O_3.	SiO_2.	H_2SO_4.	Cl.	HNO_2.	K_2ONa_2O.	substances.
13·4	8·9	3·0	4·8	3·4	0·1	traces	traces	20·0

This water is therefore of no use for medicinal purposes. D. B.

Analysis of the Water of the Schönbornsquelle at Kissingen. By E. v. GORUP-BESANEZ (*J. pr. Chem.* [2], xvii, 371—390).—Temperature of water = 19·2° to 20°. Sp. gr. at 18·5° = 1·01156. Rate of flow = 34 to 35 cubic feet per minute—

Solid Constituents.

Sodium chloride	9·50719	grams per litre.
Lithium chloride	0·01595	,,
Ammonium chloride	0·02599	,,
Magnesium chloride	0·02587	,,
,, bromide	0·00908	,,
Potassium sulphate	0·41822	,,
Calcium sulphate	0·29415	,,
Magnesium sulphate	1·15629	,,
Calcium carbonate	1·42436	,,
Magnesium carbonate	0·07329	,,
Ferrous carbonate	0·02695	,,
Manganous carbonate	0·00183	,,
Calcium phosphate	0·00303	,,
Silica	0·01344	,,

Total = 12·99624 grams per litre.

Gaseous Constituents.

Free carbon dioxide (including that present in the bicarbonate) .... = 1271 c.c. per litre
True free carbon dioxide .... = 903 c.c. ,,

Traces of cæsium, barium, strontium, aluminium, lead, arsenic, antimony, zinc (doubtful), boric and nitric acids, and bituminous organic matter were detected. M. M. P. M.

Organic Chemistry.

On Chloroform. By G. VULPIUS (*Arch. Pharm.* [3], xiii, 37).—After trial of six different sorts of chloroform, including the best, it was found that that which answered best in surgical operations was ordinary chloroform, which had, however, withstood the test of strong sulphuric acid. E. W. P.

A New Process for the Formation of Nitroethane. By P. LAUTERBACH (*Deut. Chem. Ges. Ber.*, xi, 1225).—By the distillation of equivalent quantities of potassium ethylsulphate and sodium nitrite, an oily liquid is obtained, which appears to be nitroethane, but only 6 per cent. of the theoretical quantity is produced. Ethyl nitrite and aldehyde are likewise formed at the same time. E. W. P.

Oxidation-products of β-Hexyl Iodide, Hexylene Bromide, and Monobromhexylene (derived from Mannite). By O. HECHT (*Deut. Chem. Ges. Ber.*, xi, 1420—1426).—1. *β-Hexyl iodide.*—When this compound is oxidised by a mixture of potassium dichromate and dilute sulphuric acid, it yields iodine, carbonic acid, and acetic and butyric acids; a portion is also acted upon by the free iodine, and forms a resinous product. The conclusion drawn from these results, that β-hexyl iodide has the constitution,

$$CH_3.CHI.CH_2.CH_2.CH_2.CH_3,$$

is weakened by the observation that the iodide is also decomposed when heated with sulphuric acid of the same concentration as that used in the oxidation, iodine and hydriodic acid being set free, so that the oxidation-products may result from the oxidation of hexylene.

2. *Hexylene bromide.*—The oxidation of this compound, whose constitution has been determined by the author (*Ber.*, xi, 1154), yielded similar results; butyric and acetic acids are formed, bromine is set free, and reacts on the unaltered bromide, forming further substituted compounds. When boiled with dilute sulphuric acid the bromide is resolved into hydrobromic acid and a resinous product. The sulphuric acid solution was also found to contain some hexylene glycol, $C_6H_{12}(OH)_2$, from which it would appear that the formation of this body preceded the oxidation.

3. *Monobromhexylene.*—The oxidation of this body yielded butyric

and acetic acids and bromine, which latter formed with the unaltered compound a substance having the composition, $C_6H_{10}Br_2$. Monobromhexylene is unattacked by dilute sulphuric acid, so that the reaction is a direct oxidation. It does not, however, decide between the two possible constitutional formulæ—

$$CH_3.CBr{=}CH.CH_2.CH_2.CH_3 \text{ and}$$
$$CH_3.CH{=}CBr.CH_2.CH_2.CH_3,$$

as both would yield butyric and acetic acids.

The author infers that, in the oxidation of such bodies, the halogen atom is set free, whilst the carbon-atoms united to it are resolved into carboxyl groups, and in other respects the chains of carbon-atoms are oxidised in accordance with Popoff's law. The method of limited oxidation may therefore be used to determine the constitution of such halogen derivatives. P. P. B.

Preparation of Ethylene and Ethylene Compounds. By E. ERLENMEYER (*Liebig's Annalen*, cxcii, 244—255).—The author criticises Demole's objection (*Annalen*, clxxxiii, 123) to the apparatus described by Bunte and himself, in 1873, for preparing ethylene and ethylene bromide (*ibid.*, clxviii, 64), and in turn points out objections to the apparatus of Demole, whilst upholding the efficiency of his own: he has slightly modified the proportions, however, allowing a mixture of 1 part alcohol with 2 of sulphuric acid to flow into the mixture of 25 grams alcohol with 150 grams sulphuric acid.

Demole's method (*ibid.*, clxxvii, 45) for preparing glycol, by the action of potassium acetate on ethylene dibromide, has been carefully examined by the author. He finds that the formation of glycol by this method attains a maximum when the proportion of water present is such that, on the one hand, the monacetin formed is completely saponified, and, on the other, at least the greater part of the acetic acid set free in the reaction is taken up by the alcohol with production of ethylic acetate.

From his experiments upon the method of Zeller and Hüfner (potassium carbonate solution and ethylene bromide), the author believes that the production of glycol takes place in two stages—

$$\text{(1.) } CH_2Br.CH_2Br + 2(KO.COOK) = CH_2(O.COOK).CH_2(O.COOK) + 2KBr.$$

$$\text{(2.) } CH_2(O.COOK).CH_2(O.COOK) + 2HOH = CH_2(OH).CH_2(OH) + 2(HO.COOK).$$

A third reaction, resulting in the production of C_2H_3Br, also takes place. This may be probably formulated as—

$$CH_2Br.CH_2Br + KO.COOK = CH_2{=}CHBr + KBr + HO.COOK.$$

Zeller and Hüfner add alcohol, in order to precipitate the potassium bromide formed during the reaction. The author recommends a mixture of equal parts of alcohol and ether, and suggests the advisability of saturating the alcoholic ethereal liquid with carbon dioxide, in order to decompose the potassium alcoholate which, from his experiments, seems to be formed. The method recommended by the author for the preparation of monacetin and glycol is based upon that of Atkinson (*ibid.*, cix, 232), and is as follows:—

600 grams ethylene bromide, 700 grams fused potassium acetate, and 1,500 to 1,800 grams alcohol, of 0·83 sp. gr., are boiled together in a flask fitted with an upright condenser, until the bromide ceases to be precipitated from the alcoholic liquid by addition of water. When cold, the liquid is passed through a filter, to separate potassium bromide, and is then distilled. The portion which passes over above 140° (400 to 440 grams) is warmed for 12 hours on a water-bath, with excess of barium hydrate dissolved in boiling water. The strongly alkaline liquid is then saturated with carbon dioxide, filtered, and evaporated to one-third of its bulk on the water-bath. The residue, after cooling, is washed into a flask with a weighed amount of very strong alcohol, an equal weight of ether is added, and the whole is well shaken. The clear liquid is withdrawn from the crystalline precipitate, the residue washed with a mixture of equal weights of alcohol and ether, the washings passed through a filter, and the whole liquid heated on a water-bath, until the alcohol and ether are removed; the residual liquid is then fractionated, the portion boiling above 186° being kept separate. That which boils below 186° is boiled down to a syrupy consistence on the water-bath, and is then again fractionated. About two-thirds of the theoretical yield of glycol is obtained by this process. M. M. P. M.

Oxidation of Unsaturated Chloro-, Bromo-, and Chlorobromo Substituted Hydrocarbons. By E. DEMOLE and H. DÜRR (*Deut. Chem. Ges. Ber.*, xi, 1302—1306).—One of the authors has already shown that dibrom- and tribromethylene, when treated with free oxygen, yield brom- and dibromacetyl bromide (*Ber.* xi, 315). The bodies, $CH_2{=}CHBrC_2Cl_4$, and C_2Br_4, when treated with free oxygen in presence of platinum black, are not oxidised at all. Dichlorethylene, $C_2H_2Cl_2$, which Regnault has shown to undergo polymerisation when exposed to the air (*Ann. Phys. Chim.*, lxix, 157), is found to undergo a similar change, with evolution of acid vapours when shaken up with free oxygen.

The compound, $CHCl{=}CHBr$, which Müller (*Annalen, Sup.* iii, 287) prepared by the action of potassium cyanide on $C_2H_3ClBr_2$, solidifies easily, forming a polymeric modification. This compound when shaken up with oxygen, yields a large quantity of a fuming liquid, boiling at 128°—132°, and a small quantity of an oily liquid, boiling at 140°, besides some unaltered $CHCl{=}CHBr$. The liquid boiling at 128—132°, is a mixture of bromacetyl chloride and chloracetyl bromide, as is shown by its boiling point, and also by its yielding with water, brom- and chloracetic acids, and with alcohol, ethyl brom- and chloracetates, together with hydrochloric and hydrobromic acids. The oily liquid boiling at 140° is a polymeric modification of C_2H_2ClBr, which solidifies on exposure to the air, and carbonises when heated above 100°.

Bromamylene, which contains the group CHBr, when treated with free oxygen, is unaltered. From these experiments the authors conclude that—1. If a bromo-, chloro-, or chlorobromo-substituted ethylene undergoes polymerisation on exposure to the air, that it absorbs oxygen, and forms an acid compound. 2. If polymerisation does not take place, oxidation cannot. 3. The final products, C_2Cl_4 and C_2Br_4, since they contain no hydrogen, can neither be oxidised, nor do they form polymerides. 4. The bromo-substitution compounds of series homologous with the ethylene series, do not appear to form polymerides, or to be oxidised by free oxygen. P. P. B.

Experiments and Theory on the Change of $CHBr{=}CHBr$ by means of Oxygen into $CH_2Br{-}COBr$. By E. DEMOLE (*Deut. Chem. Ges. Ber.*, xi, 1307—1314).—The author first gives an account of a series of experiments undertaken to explain the different parts played by oxygen, moisture, and temperature in their action on dibromethylene, $C_2H_2Br_2$. This substance, when sealed up with dry air, undergoes little change, a solid polymeride forming in small quantities only; when exposed to the action of moist air it, however, partly solidifies, and partly remains liquid. The former portion is a polymeric modification, the latter contains monobromacetic acid and $C_2H_2Br_4$, which boils at 200°. When a current of moist air is passed through $C_2H_2Br_2$, then it is chiefly changed into solid polymerides, scarcely any bromacetic acid, and very little bromacetyl bromide being produced. If the air be dry and the temperature 15°, the quantity of the polymeric modification is less, but the quantity of acid bromide is increased; if the temperature be raised to the boiling point, then no solid modification is formed, but a large quantity of bromacetyl bromide. If a current of dry oxygen be passed into dibromethylene, at first a little of the solid modification is formed, but when the temperature rises the acid bromide is alone formed. If, however, water be present, and the temperature allowed to rise to 50°, then one half of the dibromethylene is changed to the oxidation-product, the other half to the solid product; whereas, if the temperature be kept at 15—20°, then three-quarters are resolved into the solid modification. The observations of Lennox (this Journal, xiii, 206), show that ethylene tribromide on exposure to air polymerises, dibromacetic acid being formed at the same time.

From these experiments it will be seen that oxygen is necessary to polymerisation, and that the presence of water also favours it; whilst if the temperature be allowed to rise to 50°, the oxidation-product is formed alone. Dibromethylene dissolved in benzene, and exposed to the action of air, forms the polymeride only, whilst its alcoholic solution yields bromacetic ether and a little $C_2H_2Br_4$.

To explain this action the author supposes that first the ethylene dibromide is resolved into hydrobromic acid and an unsaturated compound, $CHBr{=}C{=}$. This body unites with hydrobromic acid, and forms the polymeric compound, thus:—

$$CHBr{=}C{=} + HBr = n(CHBr{=}CHBr).$$

Again when acted upon by HBr and oxygen it forms the acid bromide, as follows:—

$$CHBr{=}C{=} + HBr + O = CH_2Br.COBr.$$

It is also possible that some hypobromous acid is formed, which reacts on the $C_2H_2Br_2$, forming $C_2H_2Br_4$. Similarly the oxidation of $CHCl{=}CHBr$ may be explained, HCl and HBr, together with $CH_2Br.COCl$ and $CH_2Cl.COBr$, being formed. $CH_2Br.COCl$ occurs in larger quantity than $CH_2Cl.COBr$, since $CHCl{=}$ is less stable than $CHBr{=}$. The decomposition of tribromethylene is explained by the following equations:—

$$(1.)\quad CHBr{=}CBr_2 = CBr_2{=}C{=} + HBr.$$

$$(2.)\quad CBr_2{=}C{=} + HBr = \underset{\text{Polymeric compound.}}{n(CHBr{=}CBr_2)}.$$

$$(3.)\quad CBr_2{=}C{=} + HBr + O = \underset{\text{Dibromacetyl bromide.}}{CHBr_2.COBr}.$$

From this theory it will be seen that $CHBr{=}CH_2$ may undergo oxidation and polymerisation, whereas such bodies as C_2Cl_4 and C_2Br_4 cannot, since they contain no hydrogen. P. P. B.

Formation of Tertiary Amines by the Synthesis of Organic Acids. By E. Schmidt (*Deut. Chem. Ges. Ber.*, xi, 728—733).—In the synthesis of isobutyl-formic acid from isobutyl cyanide, which had been prepared by the action of potassium cyanide on isobutyl iodide, the author was surprised to find a considerable quantity of almost pure tri-isobutylamine hydrochloride in the residue after distilling off the alcohol. No satisfactory explanation of the formation of secondary and tertiary amines by the synthesis of organic acids has yet been given, although their production in this manner is not new, as Lieben and Rossi have thus obtained butylamine and a small quantity of di- and tributylamine as bye-products from valerianic acid (this Journal, 1873, 367), and Linnemann, ethylamine, di- and tri-ethylamine, in considerable quantity, from propionic acid. This chemist ascribed the formation of the tertiary base to the decomposition of the ethyl cyanide by hydrochloric acid, but this supposition is not tenable, as Hofmann and Gautier have shown that the isonitril is decomposed by hydrochloric acid into the primary amine and formic acid.

The greater part of the amines produced by the synthesis of organic acids undoubtedly arise from the decomposition of the isonitril which is always formed together with the normal nitril, by the action of potassium cyanide upon the iodide of the alcoholic radicle; and the author confirms Gautier's statement that the isonitril is decomposed by the continued action of alcoholic potassium hydrate into a primary amine and formic acid; and, further, it was found that by continuing the action for a period of six weeks, it was impossible to convert the primary amine into a secondary or tertiary base. It is to be remarked, therefore, that the isobutylamine which accumulates in the alcoholic liquors when the same alcohol is continuously used in the preparation of isobutylformic acid, could not have been converted into the tertiary base in this manner. The author explains the production of the tri-isobutylamine by accumulative action, arising on the one hand between the ammonium hydrate which is formed by the decomposition of the cyanate contained in the potassium cyanide, and a part of the isobutyl-iodide, thus forming primary, secondary, and tertiary amines, and, on the other hand, by the production of a mixture of amine bases, valeronitrile, valeronisonitrile, &c., when the alcoholic solution of the crude isobutyl-cyanide was heated for two days with potassium hydrate, plus the isobutylamine formed from the isonitrile as above stated. On again using the alcohol in the preparation of the organic acid, the primary and secondary amines contained therein would be converted into tertiary amines by contact with the excess of isobutyl iodide. The results of Lieben and Rossi, also those of Siersch, are attributed to a similar reaction.

The author disputes Linnemann's statement that the tertiary amines are formed by the action of hydrochloric acid on the ethyl cyanide, and shows that the di- and tri-ethylamines which were obtained by Linnemann, were the products of the dry distillation of potassium ethylsulphate with potassium cyanide, inasmuch as it is known that crude potassium cyanide yields ammonium hydrate and carbonate by dry distillation, and that he has found that both methyl- and ethyl-potassium sulphates give a considerable quantity of primary and tertiary bases (presence of secondary bases not so certain) by dry distillation with ammonium carbonate.

The dry distillation of potassium methylsulphate gives more tertiary than primary amine, whilst the contrary result ensues in the case of potassium ethylsulphate. Boiling these salts with ammonium hydrate (20 per cent. solution) partly converts them into primary and tertiary amines. This action is only to be ascribed to the combination of the ammonia with the alcohol at the moment it is expelled from the ethereal sulphates. The presence of the amines in wood-spirit is more probably due to this action than to the action of the ammonia on acetone, as supposed by Vincent, for Heintz has shown that if this were so, acetone bases would be formed, and not aldehyde and methylamine, which is the case. A. J. C.

Tri-isobutylamine. By R. SACHTLEBEN (*Deut. Chem. Ges. Ber.*, xi, 733—734).—The author has examined the tri-isobutylamine which was obtained by Schmidt, as described in the above paper. The analysis of the platinum salt gave numbers corresponding to—

$$[N(C_4H_9)_3]_2PtCl_6.$$

The free base was prepared by decomposition of the hydrochloride with potash, then purified by distillation and dried by ignited potassium carbonate. The boiling point of tri-isobutylamine lies between 184° and 186° (uncorrected). Normal tributylamine boils at about 208° (Lieben and Rossi), and isobutylamine between 65·8° and 68·3° (Linnemann). It is a transparent, mobile liquid, with sp. gr. 785 at 21°, and possesses a strongly ammoniacal smell. On account of their hygroscopic character and their great solubility in water, the nitrate, hydrochloride, sulphate, and phosphate crystallise with difficulty. Needle-shaped crystals have, however, been obtained by allowing a syrupy solution of one of these salts to stand for some time over sulphuric acid, but the crystals soon disappear on exposure to air.

A crystalline anhydrous platinum salt has been obtained: it separates from cold water in very fine orange-red crystals similar in crystalline form to ammonium chloride. The gold salt has the composition $N(C_4H_9)_3HCl.AuCl_3$. A salt crystallising from hot water in brilliant needles is prepared by neutralising the base with oxalic acid. When tri-isobutylamine is heated with an equivalent quantity of isobutyl iodide for two days at 120—130° in a sealed tube, the entire liquid solidifies on cooling to a radiated crystalline mass, which may be described as tetra-isobutyl-ammonium iodide.

A. J. C.

Phytosterin and Cholesterin. By O. HESSE (*Liebig's Annalen*, cxcii, 175—179).—By extracting powdered Calabar beans with petroleum ether, and evaporating, an oily residue is left, which after a time solidifies to a butyraceous mass of crystals. On pressing this between bibulous paper to remove the oil, and dissolving the residue in hot alcohol, and recrystallising from ether and alcohol successively, brilliant colourless tabular crystals are obtained which melt at 132—133°, and give numbers on analysis agreeing with the formula $C_{26}H_{44}O.H_2O$. By recrystallisation from petroleum ether, the substance is obtained in needles which contain no water of crystallisation.

A solution of "phytosterin" in chloroform shows left-handed polarisation, $(\alpha)_D = -34{\cdot}2°$ at 15°. Phytosterin seems to be identical with Kolbe's "cholesterin from peas."

Cholesterin, obtained from gall stones, crystallises from alcohol and from chloroform in forms the same as those assumed by phytosterin, but the crystals obtained from an ethereal solution consist for the most part of tables. Cholesterin melts at 145—146°.

Dehydrated cholesterin in chloroform solution gave a left-handed polarisation, $(\alpha)_D = -(36{\cdot}61 + 0{\cdot}249\,p)$. The author is inclined to regard cholesterin as the next lower homologue of phytosterin, viz., $C_{25}H_{42}O$, and believes it probable that the two substances occur together in the animal kingdom.

M. M. P. M.

Preparation of Glycol. By S. STEMPNEWSKY (*Liebig's Annalen*, cxcii, 240—242).—Zeller and Hüfner (*J. pr. Chem.* [2], ii, 229) found that ethylene bromide is decomposed by the action of a dilute solution of potassium carbonate, with production of glycol. The author supposed that the decomposition might probably be due to the presence of potassium hydrate produced by the action of water upon the carbonate. He finds, however, that no glycol is formed by boiling ethylene bromide with an aqueous solution of potassium hydrate. Monobromethylene, C_2H_3Br, and hydrobromic acid are the products of the reaction. The same substances are also formed, although in much smaller quantity, when potassium carbonate is used in place of the hydrate. Sodium carbonate may be substituted, but not advantageously, for the potassium salt in the production of glycol from ethylene bromide; but with barium carbonate no glycol is formed.

M. M. P. M.

Action of Potash Solutions on Glycogen. By VINTSCHGAU and DIETL (*Pflüger's Archiv. f. Phys.*, xvii, 154—164).—The glycogen employed was prepared from liver by Brücke's method: it was free from nitrogen, and contained only a very small quantity of mineral matter. When a solution of glycogen was treated for 10 or 15 months with a

1 to 2 per cent. solution of potash, it lost its opalescence. The addition of alcohol to this solution did not throw down the whole of the glycogen originally present. A similar result was obtained after 10 or 15 days' action if the temperature was maintained at 50° to 60°. The precipitate obtained by addition of alcohol to the liquid produced by the action of dilute potash solution on glycogen is called by the authors *β-glycogen-dextrin.* It differs from ordinary glycogen in that it is less completely precipitated by alcohol, that its solution is entirely without opalescence under ordinary conditions, and shows but a faint bluish-white colour by transmitted light, and that it is possessed of a rotatory power different from that of ordinary glycogen. Rotatory power of ordinary glycogen, according to Luchsinger, = 130°, according to Boehm and F. A. Hoffmann = 226·7°; rotatory power of *β-glycogen-dextrin* = 195°.

The authors have not been able to detect any difference between the glycogen-dextrin of Kühne and the substance obtained as described above; but inasmuch as they do not regard the identity of these bodies as established, they have adopted provisionally the name *β-glycogen-dextrin* for the substance which they have prepared from glycogen.

The authors have attempted to arrive at a formula for glycogen and for β-glycogen-dextrin from results of analyses, but without success. The percentage of carbon found varied from 43·04 to 43·90, and that of hydrogen from 6·3 to 7·1. M. M. P. M.

On Phlorose. By O. HESSE (*Liebig's Annalen*, cxcii, 173—174). —The author obtains this sugar by acting on phlorizin with sulphuric acid according to Schiff's method. The carefully purified substance gave on combustion results corresponding with the formula $C_6H_{14}O_7$. Phlorose contains one molecule of water of crystallisation, which is expelled with difficulty between 80° and 100°; it melts at about 74°, and is as active a reducing agent as glycose.

The crystallised anhydride cannot be obtained from phlorose as is the case with glycose; another marked difference between the two is that phlorose only causes the plane of polarised light to rotate $\frac{5}{6}$ths as much as glycose. The author concludes by remarking that it still remains to be proved whether the sugar obtained from phlorizin by this method is identical with phlorose; the fact that glycose cannot be converted into phlorose by the action of sulphuric acid seems to show that Stas's sugar is not glycose; on the other hand the author points out that the rotative power of glycose gradually diminishes.

J. M. T.

Behaviour of Chlorinated Ethyl Formate with Potassium Cyanate. By T. WILM (*Liebig's Annalen*, cxcii, 243—244).—Chlorinated ethyl formate and potassium cyanate in alcoholic solution easily react upon one another, with production of ethyl allophanate and carbonate. Cyanuric acid was also obtained on distilling an ethereal solution of the crude carbonic ether. The reaction is probably:—

$$2ClCOOC_2H_5 + 2KCNO + 3C_2H_5OH = 2KCl + 2(C_2H_5)_2CO_3 + C_2H_3N_2O_3.C_2H_5.$$

The author was in hopes that a compound analogous to diglycolamic acid would have been formed thus:—

$$Cl.COOC_2H_5 + KCNO + C_2H_5.OH = NH(COOC_2H_5)_2 + KCl.$$

M. M. P. M.

Constitution of the Vapour of Acetic Acid. By A. HORSTMANN (*Deut. Chem. Ges. Ber.*, xi, 1287—1295).—From the observations of Wanklyn and of Berthelot, it follows that in fractional distillation the amount of volatile liquid in the distillate is determined by the vapour-density and tension of its vapour. This holds also in other distillations, so that if the absolute quantity of vapour passing over, and the tension at that temperature are known, the vapour-density may be determined. On this principle the author has perfected a method by which he has determined the quantity of acetic acid distilling over in a current of air at low temperatures, and the observations of Landolt (*Annalen, Supp.*, xi, 129) furnishing the tension of its vapour at these temperatures, the vapour-density at temperatures ranging from 15—49° has been determined. These results show that the vapour-density varies from 1·85—2·89, values approaching the normal one 2·03. The author considers that these results do not warrant the view that the abnormal vapour-density of acetic acid is due to the existence in the state of vapour of a polymeric modification of acetic acid, which is not completely resolved until heated to 250°. The anomalous vapour-density of acetic acid is to be viewed rather as analogous to those cases of other bodies whose vapour-density is always greater at temperatures near the boiling point.

P. P. B.

Action of Trichlorolactic Acid on Urea (Preliminary Notice). By C. O. CECH (*Deut. Chem. Ges. Ber.*, xi, 726—728).—The substance, which the author prepared by mixing together, in the cold, dilute solutions of chloral hydrate and potassium cyanide (this Journal, 1876, i, 376), may be regarded as urea in which one atom of hydrogen is replaced by trichlorlactyl. It seemed probable, therefore, that trichlorolactyl urea would be produced by the action of trichlorolactic acid on urea. It is found, however, that the reaction occurs in quite a different manner. When these two substances are mixed together in an aqueous solution, no action takes place, but if the crystalline trichlorolactic acid be added to the melted urea, and the mixture cooled to prevent carbonisation, there is a strong reaction, with formation of hydrochloric acid and carbon dioxide, and separation of a white vesicular mass, which is insoluble in alcohol and in ether, but readily dissolves in hot water, from which it can be crystallised in white silky laminæ. The excess of urea and trichlorolactic acid, and the hydrochloric acid formed during the reaction, can be separated by washing the crystals with alcohol and cold water, then recrystallising from hot water.

This new body, which has no fixed melting point, but carbonises at 203°, appears to be produced by the action of two molecules of urea on one molecule of trichlorolactic acid, and to be represented by the formula $C_4H_8Cl_2N_4O_2$.

A. J. C.

Undecylenic Acid. By F. Becker (*Deut. Chem. Ges. Ber.*, xi, 1412—1414).—This acid, which Krafft prepared (*Ber.*, x, 2034) by the dry distillation of castor-oil, by which method a yield of 10 per cent. is obtained, has the composition $C_{11}H_{20}O_2$. It is solid at ordinary temperature, melts at 24·5°, and boils with slight decomposition at 295° under ordinary pressure, whilst under reduced pressure it boils at 200° without decomposition. The barium salt is very characteristic, and has been used to obtain the pure acid; it crystallises in shining flat needles or plates, and is difficultly soluble in water. Bromine attacks the acid dissolved in carbon bisulphide, a compound having the composition $C_{11}H_{20}Br_2O_2$ being formed. It is obtained as a hard crystalline mass, and melts at 38°. Undecylenic acid, when fused with potash, yields nonylic acid (m. p. 11—12°) and acetic acid. Nitric acid converts it into sebacic acid. P. P. B.

Undecolic Acid. By F. Krafft (*Deut. Chem. Ges. Ber.*, xi, 1414—1416).—This acid is obtained by heating dibromundecylenic acid ($C_{11}H_{20}Br_2O_2$) with alcoholic potash in sealed tubes at 180° for three hours. The potassium salt thus produced yields the acid as a white crystalline precipitate when decomposed by an acid. Undecolic acid, $C_{11}H_{18}O_2$, melts at 59·5°, and may be distilled without change under reduced pressure. It dissolves easily in ether, alcohol, and carbon bisulphide, but only with difficulty in water, from which it may be obtained in thin shining plates. With bases, undecolic acid forms in general well characterised and crystallisable salts. By fusion with potash it is converted into an acid boiling at 220—222°, which, from the analysis of its barium salt, appears to be a heptoic acid, perhaps identical with œnanthylic acid. Nitric acid acts upon undecolic acid, producing azelaic acid. P. P. B.

Preparation of Carbon Oxychloride. By E. Paternò (*Gazz. chim. ital.*, viii, 233).—The author's method consists in passing a mixture of chlorine and carbon monoxide through a glass tube 15 m.m. in diameter, and about 40 c.m. long, filled with pellets of animal charcoal. In presence of this substance the combination of the two gases takes place with great rapidity, and without the aid of sunlight. It is, moreover, accompanied by considerable disengagement of heat, rendering it necessary to keep the tube continually cool. The combination is complete even when the current of gas is very rapid; and it is easy to obtain the oxychloride free from chlorine, and containing a slight excess of carbonic oxide, by regulating the stream of gas in such a manner that the gas after combination shall be colourless. The oxychloride in this state serves well for the preparation of chloroformic ethers, and for the greater number of reactions in which it is employed. If it is to be afterwards liquefied, it is best prepared with a slight excess of chlorine, which may be afterwards eliminated by known processes.

By the aid of this mode of preparing carbon oxychloride, it is easy to obtain in a day a kilogram of ethylic oxychlorocarbonate.

H. W.

On Monorubidium Oxalate and its Preparation from Rubidium Alum. By STOLBA (*Chem. Centr.*, 1878, 331—333).—(1.) *Preparation of Monorubidium Oxalate from Rubidium Alum.*—100 grams of finely-powdered rubidium alum free from potassium, and 72·6 grams pure crystallised oxalic acid, also free from potassium, are heated to boiling in a platinum dish, together with 170 c.c. of water. As soon as the solution is complete, it is allowed to cool, and occasionally stirred, so that the deposition of crystals may be as complete as possible. When no more crystals can be observed to form, the solution, and afterwards the crystals, are poured into a funnel stopped with a plug of clean cotton wool, and filtered under pressure; the crystals are then washed with the smallest possible quantity of water several times, and dissolved in four times their volume of boiling water; while cooling, the liquid is stirred continually so as to obtain small crystals, which are again filtered and washed. They are then carefully tested for sulphuric acid, and even if they should be found to be free from it, it is advisable to recrystallise, when a perfectly pure product is obtained, unless the rubidium alum contained cæsium, when it must be repeatedly recrystallised until no trace of cæsium is found in the crystals by the spectroscope. The first mother-liquor gives some of the salt mixed with oxalic acid on careful evaporation, which, if carried too far, would cause the deposition of aluminium sulphate. To recover the small quantity of rubidium still contained in the mother-liquor, it is evaporated to dryness, and then heated until the free sulphuric acid is expelled and the mass begins to crumble; by this means the whole of the oxalic acid is decomposed. The residue is then taken up in a sufficient quantity of hot water, and on standing the rubidium alum separates out, as it is practically insoluble in a solution of the aluminium sulphate.

(2.) *Analysis of Monorubidium Oxalate.*—The rubidium oxide was determined by strongly heating a weighed quantity of the salt, and titrating the carbonate obtained. The total oxalic acid was determined volumetrically in the usual way, and the oxalic acid which could be estimated by neutralising with titrated alkali was also found, phenolphthaleïn being used as indicator, which, the author states, gave satisfactory results. The loss at 100° C. was determined by means of the air-bath. The numbers found lead to the formula:—

$$RHC_2O_4 + H_2C_2O_4 + 3H_2O.$$

(3.) *Properties of Monorubidium Oxalate.*—Separate crystals of this body are obtained by allowing a cold solution to evaporate spontaneously. The crystals so obtained are fine, transparent, many-sided prisms, which, like those of the similar potassium compound, appear to belong to the triclinic system. When a concentrated hot solution is allowed to cool, translucent, foliated, crystalline aggregates are formed. Both kinds, when dried at 100°, become milk-white, and do not seem to be deliquescent in dry air. The sp. gr. of the powdered salt at 18° is 2·1246. Its solubility increases with the temperature. It easily forms supersaturated solutions, as is still more the case in the analogous cæsium compound. No decomposition takes place on solution in water. The density of the saturated solution at 21° was 1·0111. The salt is very difficultly soluble in alcohol. On heating to redness, it is converted into carbonate, which, when obtained from the pure salt, does not attack platinum.

(4.) *On the use of Monorubidium Oxalate in the formation of other Rubidium-compounds.*—The fact that careful heating converts the salt into the carbonate, from which many rubidium-compounds may be formed, shows how useful this salt is. By acting on it with certain lead and silver salts, also, many compounds of rubidium may easily be formed. For these reactions, dirubidium oxalate is in some cases the better salt to use; it is prepared by neutralising the monorubidium oxalate with carbonate of rubidium. Monorubidium oxalate containing cæsium may also be used for producing pure rubidium-compounds, by converting it first into carbonate and then into chloride.

J. M. T.

Introduction of Cyanogen Groups into Organic Compounds, and Decomposition of Organic Cyanides. By A. CLAUS (*Liebig's Annalen*, cxci, 33—93).—By experiments made in conjunction with Kölver (*Annalen*, clxx, 126) some years ago, the author showed that when potassic cyanide acts upon dichloroglycide, a cyanide is produced, which by saponification yields *tricarballylic acid;* this result being due to the fact that, besides the substitution of cyanogen for chlorine, assimilation of hydrocyanic acid takes place. This investigation has been extended to other non-saturated bodies, and the author is now enabled to prove that such an assimilation of hydrocyanic acid occurs only when the CN group at the same time displaces a halogen, and even then not always. Moreover, addition of HCN does not always take place in the manner indicated by theory, but follows totally different laws. By his experiments the author is also led to the conclusion that under no circumstances can more than one cyanogen group be added to a single carbon atom; and that when the attempt to do so is made, either there is no reaction, or intramolecular transposition or molecular dissociation occurs. The author doubts the correctness of the statement of Pfankuch (*Jour. pr. Chem.*, vi, 97, 1872) that cyanoform is produced by the action of mercuric cyanide on iodoform, as he has been quite unable to obtain either cyanoform or the compounds of it described by Pfankuch. The existence of another tricyanide mentioned by Orlowski (*Ber.*, ix, 1604) as a constituent of the double salt, $C_2H_3(CN)_3.(AgCN)_3$, has not been satisfactorily established.

Many observations, however, including those of the author on the action of potassic cyanide upon chloromaleic ether, show that addition of HCN is not prevented by the presence of carboxyl groups; although it is not always possible to convert the cyanogen into a carboxyl group, separation easily taking place.

When 1 mol. allyl iodide and 2 mols. potassic cyanide in alcoholic solution are heated at 110° for two or three days, and the mixture subsequently boiled for six or seven days with caustic potash, *crotonic* and *pyrotartaric* acids are produced. The intermediate cyanides could not be isolated. This pyrotartaric acid, when heated for a long time at 200—210°, splits up, partly into carbonic anhydride and butyric acid, partly into water and pyrotartaric anhydride. These modes of decomposition, singular in so far as they take place together, the author finds also to belong to Arppe's pyrotartaric acid (methyl-succinic acid, $CH_3.CH(COOH).CH_2(COOH)$, from tartaric acid), and a comparison of the salts of the two acids has proved them to be identical.

Neither *monochloropropylene* nor *methylchloracetol* (acetone chloride), $(CH_3)_2CCl_2$, when treated under various conditions with potassium cyanide, the products being subsequently boiled with potash, yielded any trace of an acid, contrary to what might have been expected if the behaviour of dichloroglycide and allyl iodide were characteristic of all halogenised compounds containing the grouping $C{=}C$.

Trichlorobutyric ether (formerly regarded as trichlorocrotonic ether), which the author believes to contain the grouping CCl_2, when boiled with potassic cyanide and caustic potash, also yields only gaseous products, but no acid of higher basicity.

Trichloracetic ether, dissolved in *aqueous* alcohol and similarly treated, furnishes potassic chloride, acetic acid, and potassic and ammonic carbonates. In the absence of water, however, the cyanide acts like a feeble alkali and chloroform is produced.

When *chlorocrotonic ether* is boiled with two equivalents of potassic cyanide dissolved in spirit, potassic chloride separates after five or six hours. If this salt be removed and the residue boiled with potash as long as ammonia escapes, and the product treated with sulphuric acid and ether, an uncrystallisable substance is extracted. This substance, when redissolved and precipitated with lead acetate and the precipitate decomposed by sulphuretted hydrogen, is again obtained as an uncrystallisable mass, soluble in ether. If, however, it is dried for a long time on the water-bath, it loses its property of being completely soluble in ether. The *insoluble* portion, by the addition of a little water, is again rendered soluble in ether, and on evaporation is obtained as *tricarballylic acid.* The portion of the dried residue *soluble* in ether, when dissolved in water, neutralised with potassic carbonate and fractionally precipitated with silver nitrate yields, besides tricarballylic acid, a dibasic acid, apparently $C_3H_4(COOH)_2$, named by the author *crotaconic acid.* It is isomeric with itaconic citraconic, and mesaconic acids. The following is a simpler method of obtaining it:—Two equivalents of potassic cyanide dissolved in diluted alcohol are allowed to act *in the cold* upon one of chlorocrotonic ether. Potassic chloride gradually separates, and on evaporating the filtered liquid, taking up with strong alcohol and adding ether, *potassic cyanocrotonate* separates in small, hard, white crystals, which evolve ammonia when boiled with potash. The corresponding silver salt is unstable, and free cyanocrotonic acid on contact with water changes into acid *ammonium crotaconate*:

$$C_3H_4(CN)COOH + 2H_2O = C_3H_4(COONH_4)COOH.$$

Pure crotaconic acid is easily soluble in water, alcohol, and ether, from which menstrua it is deposited in crystals: these melt at 119° to a syrup which at 93° solidifies to a glassy mass. When moistened with water this mass again becomes crystalline. Various salts of it are described. Crotaconic acid is distinguished from its isomerides by decomposing at 135—140°. With hydrobromic acid it easily forms an addition product melting at 141°, probably bromethylmalonic (bromo-pyrotartaric) acid, $C_3H_5Br(COOH)_2$.

From these experiments it is clear that addition of HCN to chlorocrotonic ether takes place at boiling heat, but not in the cold.

In preparing *chloromaleic ether* for their experiments the authors have not found Henry's method (treatment of tartaric ether with phosphorus pentachloride) advantageous. It is best obtained by the action of alcohol on chloromaleic chloride. Full details are given. The ether has a sp. gr. of 1·178 at 20°, and boils at 243—245°. Its chemical constitution is uncertain. Heating its solution in absolute alcohol with potassic cyanide led to no result; but a mixture containing 1 part of the cyanide (3 mol.) dissolved in two parts of water, 1 part of the ether (1 mol.), and so much alcohol as to produce a clear solution, becomes warm spontaneously and deposits potassic chloride. The mother-liquid when boiled with potash, strong or dilute, yielded only a very small quantity of crystalline acid. The best result was attained by acidifying the solution with hydrochloric acid, evaporating to dryness, and exhausting the residue with ether-alcohol. The crystalline crusts deposited from the mixture were boiled for some hours with strong hydrochloric acid, and on cooling *succinic acid* separated in crystals. The acid is probably thus formed. Chloromaleic ether in contact with potassic cyanide exchanges its chlorine-atom for cyanogen, and at the same time assimilates HCN, thus forming dicyanosuccinic acid, $C_2H_2(CN)_2(COOH)_2$. When this compound is decomposed by hydrochloric acid, the tetracarboxylated acid first formed loses two molecules of carbonic anhydride and gives succinic acid—

$$C_2H_2(COOH)_4 = C_2H_4(COOH)_2 + 2CO_2.$$

None of the intermediate products could be isolated.

These experiments have also been described in the *Deut. Chem. Ges. Ber.*, vii, 101; viii, 100; ix, 223; x, 822 and 928. Ch. B.

Leucine from Young Pumpkin Plants. By E. SCHULZE and J. BARBIERI (*Deut. Chem. Ges. Ber.*, xi, 1233).—The authors have already shown (*Ber.*, x, 199, and xi, 710) that young pumpkin plants contain glutamic acids and tyrosine; they have now separated leucine as well, but in very small quantities. Tyrosine appears to be always present in all the young plants. E. W. P.

Carbothialdine and other Sulphur-compounds. By I. GUARESCHI (*Gazzetta chimica italiana*, viii, 246—255).—Carbothialdine, $C_5H_{10}N_2S_2$, was discovered in 1848 by Redtenbacher and Liebig, who obtained it by the action of carbon disulphide on aldehyde-ammonia; and E. Mulder in 1868, by treating ammonium thiocarbamate with aldehyde, obtained diethylidenammonium thiocarbamate, $NH_2.CS.SN(CH.CH_3)_2$, which he regarded as identical with carbothialdine. This view is strongly corroborated by the following experiments:—

1. Carbothialdine suspended in water and treated with potassium permanganate is instantly oxidised, with evolution of heat and formation of aldehyde, hydrocyanic acid, acetic acid, and sulphuric acid, no trace of any other sulphur-compound being formed, whereas thialdine

and thioaldehyde, in which the sulphur is directly united with the ethylidene-group, yield an acid having the composition $C_2H_4S_2O_6H_2$. The formation of hydrocyanic acid is easily explained by the well-known facts that thiocarbamic acid decomposes spontaneously into hydrogen sulphide and thiocyanate—

$$NH_2.CS.SH = SH_2 + CS.NH,$$

and that thiocyanates treated in acid solution with potassium permanganate yield hydrocyanic and sulphuric acids—

$$CS.NH + O_3 + H_2O = CNH + SO_4H_2.$$

Carbothialdine treated with water at ordinary temperatures, and then with ferric chloride, produces little or no red coloration at first; but after a short time exhibits the red colour of the thiocyanate, which subsequently disappears and gives place to a milky precipitate, the liquid then becoming deep-red on addition of ferric chloride.

If carbothialdine be boiled with water, and the liquid after cooling treated with ferric chloride, a precipitate of ferric sulphide is obtained, and on heating the liquid an odour of garlic becomes perceptible. If after the addition of ferric chloride to carbothialdine suspended in cold water, the liquid be slightly heated, the deep-red colour of ferric thiocyanate is immediately developed. Thiocarbamide and diphenylthiocarbamide on the other hand, even after boiling for a long time, do not give with water and ferric chloride the reaction of the thiocyanates, but rather that of sulphur and a ferrous salt.

These facts are inconsistent with the opinion of Claus that carbothialdine is a compound thiocarbamide. Diethylidenethiocarbamide, $CS.N_2H_2(CH.CH_3)_2$, treated with hydrochloric acid, yields ammonium chloride, aldehyde, and thiocarbamide, as shown by Nencki in 1875; and in like manner carbothialdine, if it were a thiocarbamide containing the group $(CH.CH_3)_2S$, as supposed by Claus, should decompose in a similar manner, instead of which it is known to yield ammonium chloride, aldehyde, and carbon disulphide (Redtenbacher and Liebig).

The nature of carbothialdine is, however, most clearly shown by the facility with which it is transformed into thiocarbamic disulphide, $C_2H_4N_2S_4$, a compound which, under the name of *hydranzotine* or *cyanic bisulphydrate* was described in 1843 by Zeise, who obtained it by the action of chlorine, or of hydrochloric acid and a ferric salt, on ammonium thiocarbamate. The author of this paper has obtained it in small crystals tolerably pure by treating carbothialdine with hydrochloric acid and ferric chloride, or with chlorine-water.

Thiocarbamic disulphide appears under the microscope sometimes in lozenge-shaped scales resembling uric acid, sometimes in prismatic crystals, like those of ammonio-magnesian phosphate. It is insoluble in water even when heated, but dissolves in alcohol and in ether. Boiling water decomposes it, with formation of ammonium thiocyanate, sulphur, and carbon disulphide. When heated it does not melt, but decomposes, with evolution of hydrogen sulphide and ammonium hydrosulphide, together with a yellowish-white sublimate and a trace of carbonaceous residue. On treating it with potassium permanganate, the greater part of the sulphur is oxidised to sulphuric acid, and a small portion separates in the free state.

The formation of this compound from carbothialdine may be represented by the equation—

$$\left.\begin{array}{l} NH_2.CS.SN(CH.CH_3)_2 \\ NH_2.CS.SN(CH.CH_3)_2 \end{array}\right. + 4H_2O + Cl_2 = \begin{array}{l} NH_2.CS.S \\ \quad\quad\quad\;\; | \\ NH_2.CS.S \end{array} + 2NH_4Cl + 4C_2H_4O.$$

Other formulæ which have been proposed for carbothialdine do not afford an equally satisfactory explanation of its transformation into thiocarbamic disulphide.

An alcoholic solution of carbothialdine gives a black precipitate with silver nitrate; with neutral lead acetate it first turns yellow, and then yields, slowly in the cold, a yellow precipitate changing to orange, red, and black, and blackening rather quickly when heated, with formation of lead sulphide, which is deposited in the form of a metallic speculum.

The facts above detailed show clearly that there is no relation, either of constitution or of chemical reactions, between thialdine and carbothialdine.

Thialdine and *Thioaldehyde*.—Thialdine, $C_6H_{13}NS_2$, oxidised with potassium permanganate, yields, amongst other products, sulphuric acid, acetic acid, and a sulphuretted acid whose potassium salt, $C_2H_4K_2S_2O_6$ (90 per cent. of the thialdine employed), forms white, hard, fragile lamellar crystals, inodorous even when heated, very soluble in water, less soluble in alcohol, from which it crystallises. When heated it burns with a blue flame, without previous fusion, leaving a residue of sulphur and carbon. Its solution gives with *silver nitrate* a yellowish-red precipitate, which afterwards blackens; with *mercurous nitrate*, an immediate black precipitate; with *lead acetate*, a white precipitate which does not blacken when heated; with *cupric sulphate*, a light yellow; and with *ferric chloride*, a light amethyst-coloured solution which does not become turbid when heated.

The formation of this potassium salt is not consistent with the supposition that the sulphur in thialdine is in the form of sulphydryl, SH. The same salt is obtained, though in smaller quantity (about 20 per cent.), by oxidation of thioaldehyde $(CH_3.CHS)_3$, with permanganate.

Oxysulphobenzide, $(C_6H_4.OH)SO_2$, is completely oxidised by permanganate, yielding the potassium-salt $(C_6H_4.OK)SO_2$, together with sulphate and oxalate. The potassium-oxysulphobenzide is soluble in alcohol and may be purified by crystallisation therefrom. Its solution is alkaline, and when neutralised with hydrochloric acid solidifies to a mass of shining crystals of oxysulphobenzide.

If the quantity of permanganate employed is sufficient to oxidise the whole of the oxysulphobenzide, one portion of the latter remains unattacked, and the rest is completely oxidised to sulphuric, oxalic, and carbonic acids, without formation of intermediate products.

This mode of oxidation may be conveniently applied to the exact determination of sulphur in oxysulphobenzide, and other sulphur-compounds. The oxysulpho-benzide in powder is mixed with a little water in a long-necked flask, and pulverised permanganate is added, by small portions, till the liquid remains permanently violet, heat being applied if necessary. The excess of permanganate and the manganese oxide formed are then removed by heating the liquid to boiling for a few minutes with hydrochloric acid. In the colourless liquid, filtered if necessary, the sulphuric acid is determined by the usual method.

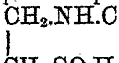
The method of oxidation with permanganate was employed by Cloez and Guignet (*Compt. rend.*, 1858, xlvi, 1110) for the estimation of sulphur in gunpowder, and has been proposed by Erlenmeyer and R. Hofmann (*Erlenmeyer's Lehrbüch d. Org. Chemie*, 171) for the estimation of sulphur in thiocyanates.

Thiocarbamide, $CS(NH_2)_2$, and *diphenyl-thiocarbamide*, $CS(NHC_6H_5)_2$, when oxidised by permanganate likewise yield all their sulphur in the state of sulphuric acid. The latter compound when thus treated gives off the odour of benzaldehyde, but the residues, C_6H_5, are difficult to oxidise.

Diphenyl-thiocarbamide is commonly said to melt at 140°, but Guareschi finds that, when purified by repeated crystallisation from boiling alcohol, it separates in very thin plates having a splendid nacreous lustre and melting at 146·5°.

Taurine, $C_2H_7NO_3S$, is oxidised with difficulty by permanganate, only a part of the sulphur (12·5 to 16·6 per cent.) being converted into sulphuric acid, instead of the calculated quantity, 25·6 per cent. Even after prolonged ebullition with excess of permanganate, part of the taurine remained unaltered, and only a very small quantity of an intermediate sulphuretted compound was obtained, possibly sulphacetic acid, $COOH.CH_2.SO_3H$.

The resistance of taurine to oxidising agents is in accordance with the fact observed by Salkowsky, that this substance, in the animal organism, is only partly transformed into sulphuric acid, the greater portion passing into the urine in the state of taurocarbamic acid,



$$\begin{array}{l} CH_2.NH.CONH_2 \\ | \\ CH_2.SO_3H \end{array}$$

H. W.

Preparation of Benzene from Brown-coal Tar Oil. By M. SALZMANN and H. WICHELHAUS (*Deut. Chem. Ges. Ber.*, xi, 1431—1434).—The formation of benzene by the action of heat on hydrocarbons, such as those contained in brown-coal tar oil, may be explained either by supposing carbon to be taken up, or hydrogen taken away, or lastly by a splitting up into two sets of hydrocarbons, one richer and the other containing less carbon. The first supposition is excluded, inasmuch as this change is always accompanied by the separation of carbon. To test the second, the authors mixed the vapours of the oil with air and oxygen before passing them through the red-hot tube, and find that the yield of benzene is not affected by it. The third appears to be the true explanation, the gas formed representing the hydrocarbons rich in hydrogen. When the vapours are passed through a heated iron tube simply, the results are not so good as when the tube is filled with such materials as asbestos, charcoal, animal charcoal, or pumice stone. By the use of such materials, and from a brown-coal tar oil, which gave off vapours at 170° and boiled at 250°, a gas was obtained which burnt in a Bunsen's burner, with a bright, reddish-white flame. The amounts of benzene varied from 3—4 per cent. of the oil used. The portion containing the benzene is also found to contain hydrocarbons boiling at 50—80°, apparently of the fatty series. P. P. B.

Decomposition of the Brown-coal Tar Oils at a Red Heat. By C. LIEBERMANN and O. BURG (*Deut. Chem. Ges. Ber.*, xi, 723—726).—In order to ascertain the possibility of utilizing some of the waste products from brown-coal tar, the authors have examined the behaviour at a red heat of the higher boiling coal-tar oils, and more especially those obtained from the brown and stone coals, as well as from "volcanic oil" and petroleum. By passing these oils through a brass tube heated to redness, either empty, or containing wood charcoal, coke, or pumice stone, it was found that all these oils, but principally those from the brown-coal tar, yielded benzene, toluene, and anthracene, and in largest quantity when wood charcoal was used.

A brown-coal tar oil of 915—920 sp. gr., which had been filtered from the paraffin after the fourth crystallisation, was purified by treatment with acid and soda, and redistillation. The purified oil, then of 885 sp. gr., and boiling at 190°, was fractionated into three parts, and gave a distillate equal to 24 per cent. at 190—280°, 48 per cent. at 280—320°, and a residue of 28 per cent., which contained a small quantity of paraffin. These three fractions were separately passed over red-hot charcoal at the rate of 80 grams per hour. The condensed products were fractionated at the temperatures of 80—120°, 120—220°, 220—310°, and above, until pitch formed in the retort. The fractions boiling at 80—120° and that over 310° were again distilled, and the amount of benzene, toluene, and anthracene determined.

The following results were obtained:—

Distillates passed over Red-hot Wood Charcoal.

Brown-coal tar-oil of 885 sp. gr. fractionated at	Condensed products per cent.	Condensed products fractionated.				
		Fraction 80—120°.	Fraction 120—310°.	Above 310°.		
		(Benzene, toluene.)	(Naphthalene, &c.)	Anthracene oil.	Crude pressed anthracene.	Pitch.
		per cent.	per cent.	per cent.	per cent.	per cent.
190—280°	48	4·0	20	12	0·8	12
280—320°	47	4·5	18	12	0·9	10
above 320°	37	3·0	12	16	1·0	8
Mean....	44	4·0	17	13	0·9	10
Brown-coal tar-oil of 889 sp. gr. not fractionated ..	45	4·6	18	12	0·7	9

The crude pressed anthracene contained 30—40 per cent. pure anthracene, according to the anthraquinone test; there was a small quantity still remaining in the "anthracene oil."

There was a greater loss from gaseous products when the tar-oils were passed through the empty, red-hot tube than when it was filled with coke or pumice stone; and it was least of all when they were passed over red-hot charcoal, in this case amounting to 56 per cent., and in the higher-boiling tar oils to 63 per cent.

The tar oil from the stone coal, when similarly treated, gave condensable products (with less loss from gaseous hydrocarbons), which amounted to 90 per cent. from a fraction boiling at 140—150°, and to 77 per cent. in another oil boiling at 160—210°. The proportion of benzene, toluene, and anthracene was very similar to that obtained from the brown-coal tar-oil.

Commercial petroleum and "volcanic" oil gave a moderate amount of benzene, scarcely any anthracene, but much loss from gaseous products.

The authors purpose investigating the subject more fully, as they consider it will perhaps be practicable to produce benzene, toluene, and anthracene from some of the comparatively worthless materials of the paraffin manufacturer.

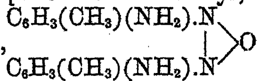
A. J. C.

Decomposition of Wood-Tar at a Red Heat. By A. ATTERBERG (*Deut. Chem. Ges. Ber.*, xi, 1222).—Tar and the less volatile tar oils, when passed over coke heated to a bright red heat, yield 7 per cent. of benzene and toluene, a small quantity of phenol, but a considerable quantity of naphthalene and anthracene, the whole representing only 25 per cent. of the original materials; whereas at a dull red heat 50 per cent. is obtained, and this consists of an easily polymerised oil (b. p. 58°), 10 per cent. of toluene containing a small quantity of benzene, phenols (b. p. 190—220°), with but little phenylic acid, and 0·3 per cent. of anthracene, naphthalene being absent. Other products were also obtained, but they were not examined. The results show that bodies rich in hydrogen yield at a red heat aromatic compounds. E. W. P.

Action of Sulphuryl Chloride on Benzene. By C. BÖTTINGER (*Deut. Chem. Ges. Ber.*, xi, 1409).—Sulphuryl chloride does not act on benzene in the cold, but does so when the mixture of the two is heated, hydrochloric acid and sulphurous acid being produced. From the product of the reaction, the author obtained a crystalline mixture of two compounds, containing sulphur and chlorine, which melted at 87—88°. He did not succeed in separating these bodies, but, from the analysis, thinks that the mixture consisted of benzene disulphide and a chloro-derivative of the same. P. P. B.

Action of Sulphuryl Chloride on Aniline. By C. BÖTTINGER (*Deut. Chem. Ges. Ber.*, xi, 1407—1408).—Sulphuryl chloride acts on aniline with considerable violence, the chief product of the reaction being aniline hydrochloride; the sulphuryl chloride is decomposed into sulphurous acid, sulphur dichloride, and chlorine. Another product of the reaction is a body containing sulphur and chlorine, which might result from the action of sulphur dichloride on aniline.

P. P. B.

Azo-compounds of Nitroparatoluidine. By E. BUCKNEY (*Deut. Chem. Ges. Ber.*, 1451—1454).—Nitroparatoluidine melting at 77·5° was prepared according to Cahours' method by reduction of dinitrotoluene (m. p. 71°) with an alcoholic solution of ammonium sulphide. If a concentrated solution of the nitroparatoluidine is treated with sodium-amalgam, in small quantities at a time, so that the reduction of 50 grams requires about two days, then azoxytoluidine is formed. Azoxytoluidine,  $$\begin{array}{l} C_6H_3(CH_3)(NH_2).N \\ \qquad\qquad\qquad\quad | \;\; \rangle O \\ C_6H_3(CH_3)(NH_2).N \end{array}$$ crystallises from hot water in small yellow needles, melting at 148°; it dissolves with difficulty in cold water, but easily in hot water and in alcohol. This base unites with hydrochloric acid to form a difficultly soluble, yellowish-brown chloride of the composition $C_{14}H_{16}N_4O.2HCl$, which forms a yellow double salt with platinic chloride, having the formula, $C_{14}H_{16}N_4O.2HCl + PtCl_4$.

Azoxytoluidine dissolved in alcohol and treated with sodium amalgam yields a mixture of azo- and hydrazotoluidine, which may be separated by taking advantage of their different solubilities in alcohol, the former being the more soluble. Azotoluidine is obtained in the crystalline state by treating its alcoholic solution with hot water. It forms red needles, insoluble in cold water, but soluble in hot water and in alcohol; it melts at 159°, and has the formula, $C_7H_6.(NH_2).N{=}N.(NH_2).C_7H_6$. Hydrazotoluidine is obtained by crystallisation from hot alcohol in small colourless rhombic plates, insoluble in water, alcohol, and ether, and difficultly soluble in hot alcohol; its alcoholic solution becomes red on exposure to the air. It melts at 180°, and has the formula,

$$C_7H_6.(NH_2).NH.NH.(NH_2).C_7H_6.$$

A moderately concentrated alcoholic solution of azotoluidine is completely converted by sodium amalgam into hydrazotoluidine.

P. P. B.

Conversion of Nitrils into Imides. By A. PINNER and F. KLEIN (*Deut. Chem. Ges. Ber.*, xi, 764—767. 3rd Paper).—By heating benzonitril with fuming sulphuric acid, Hofmann and Buckton (*Annalen*, c, 129) obtained benzene-sulphonic and benzene-disulphonic acids; similarly from acetonitril they obtained methylene-disulphonic acid.

The authors have found, however, that if benzonitril is dissolved in fuming sulphuric acid *in the cold*, and the solution poured after 24 hours into five or six times its volume of water, an abundant precipitate of *cyaphenine*, $3C_7H_5N$, is formed (m. p. 231°).

If, again, benzonitril mixed with an equal weight of benzene, is poured into sulphuric acid, kept cold, and the product diluted with water after 24 hours, only a small quantity of cyaphenine is precipitated, but on adding to the liquid soda-solution in slight excess, an abundant precipitate of a base having the composition $C_{14}H_{12}N_2O$ (m. p. 106°), is formed. This substance contains the elements of two molecules of benzonitril, plus one of water, and must have the constitution of *dibenzimide-oxide*, $NH{=}C(C_6H_5){-}O{-}C(C_6H_5){=}NH$. It crystallises in colourless prisms, which are insoluble in pure water, but soluble in dilute acids. It forms a double salt with platinic chloride. Its salts in general are unstable.

At ordinary temperatures a solution of this base in dilute hydrochloric acid gradually deposits long slender silky needles, but when boiled for a few seconds, it gives a thick mass of crystals, almost insoluble in water and dilute acids. These melt at 148·5°, and are somewhat soluble in hot water, easily in alcohol. This body is *Benzimido-benzoate*, $C_{14}H_{11}NO_2$, and is produced from dibenzimido-oxide according to the following equation:—

$$C_{14}H_{12}N_2O + H_2O = NH{=}C(C_6H_5){-}O{-}C(C_6H_5){=}O + NH_3.$$

One imide group in dibenzimide-oxide has been replaced by oxygen.

If boiled for a long time with dilute hydrochloric acid, it is completely converted into benzoic acid.

These bodies complete the transition-series from benzoic anhydride to its imide derivatives.

$O{=}C(C_6H_5){-}O{-}C(C_6H_5){=}O$, benzoic anhydride.
$NH{=}C(C_6H_5){-}O{-}C(C_6H_5){=}O$, benzimido-benzoate.
$NH{=}C(C_6H_5){-}O{-}C(C_6H_5){=}NH$, dibenzimide oxide.
$NH{=}C(C_6H_5){-}NH{-}C(C_6H_5){=}NH$, dibenzimido-imide.

The authors intend extending their experiments to the fatty nitrils. Already a benzimido-acetate, $NH{=}C(C_6H_5)-O-C(CH_3){=}O$ (*Ber.*, xi, 9), has been formed by the action of acetic anhydride upon benzimide ether. Ch. B.

Action of Fused Alkalis on Benzenesulphonic Acid. By P. Degener (*J. pr. Chem.* [2], xvii, 394—403).—The sodium and potassium salts of benzenesulphonic acid were fused with potash and soda in a silver dish over a low flame, the mass being stirred with a glass tube within which a thermometer was sealed. The proportions used were molecular, and varied from one to six molecules of the alkali to each molecule of the salt. Mixtures of potash and soda were also employed. The temperatures varied from 210 to 360°. The reaction is formulated as—

$$C_6H_5.SO_3H + 2MOH = C_6H_5.OH + M_2SO_3.$$

The amount of phenol produced was determined, after removing the metallic sulphite, by the author's volumetric method.

With potash, the amount of phenol produced increases proportionally to the increase of temperature and the mass of alkali employed. The amount of phenol produced also increases with increase of alkali and of temperature when soda is employed, but the absolute amount of phenol formed is much less than in the case of the potassium salt. With a mixture of the two alkalis, the same relation between temperature, mass, and increase of phenol produced holds good; the amount of phenol formed is larger than when soda alone is used, but is less than the mean of the results with potash and soda alone.

M. M. P. M.

Azobenzene-sulphonic Acids. By A. Pinner and F. Klein (*Deut. Chem. Ges. Ber.*, xi, 762—764).—The remarkable decomposition of nitronaphthalene-sulphonic acid into sulphuric acid and naphthylamine by the action of nascent hydrogen, has induced the authors to commence the study of α-azobenzene-sulphonic acid from α- (*meta*) nitrobenzene-sulphonic acid (m. p. of chloride, 61°; of amide, 161°). The acid is best obtained by reducing barium nitrobenzene-sulphonate with sodium amalgam. On acidifying the alkaline mixture with acetic acid and concentrating, barium azobenzene-sulphonate crystallises in yellow crusts, which retain sodium with great obstinacy. By accurately precipitating a solution of this salt with sulphuric acid, *azobenzene-sulphonic acid* is obtained, in fine, brilliant yellow needles, which dissolve in water and alcohol, but not in ether. It has not, however, been obtained free from fixed impurities.

By heating with phosphoric chloride, it is converted into a chloride which crystallises from ether in brilliant reddish-yellow plates melting at 145°. But even from this body, the acid could not be obtained pure. Alkalis convert it in great part into a resinous mass.

By dry distillation, barium azobenzene-sulphonate yields, besides *azophenylene*, a sulphuretted body, *azobenzene-sulphydrate*, which forms with mercuric chloride a crystalline mercury compound soluble in alcohol. Ch. B.

Di-imidophthaleïn of Phenyl. By A. BAEYER and J. B. BURKHARDT (*Deut. Chem. Ges. Ber.*, xi, 1297—1299).—The authors find that aqueous ammonia acts very easily at high temperatures upon phenol-phthaleïn, producing di-imidophthaleïn, to which they attribute the constitution, $C_6H_4\left\{\begin{matrix}C.NH.C_6H_4.OH\\ C.NH.C_6H_4.OH\end{matrix}\right.$, since it possesses no basic properties, which would have been the case if the amido groups had replaced the hydroxyl groups. Di-imidophthaleïn crystallises from a mixture of alcohol and benzene in colourless small sharp needles; it is slightly soluble in hot water, easily in alcohol, acetone, and glacial acetic acid, and almost insoluble in benzene and chloroform. When heated to 260° it becomes red, and melts at 265—266°. Heated in sealed tubes with hydrochloric acid at 100° it is resolved into ammonia and phenolphthaleïn.

Tetrabromodi-imidophthaleïn is prepared from tetrabromophthaleïn by the action of aqueous ammonia. It crystallises from alcohol in colourless, short needles, which melt at 280°; heated with acetic anhydride, it yields a tetracetyl compound—

$$C_6H_4\left\{\begin{matrix}CN(C_2H_3O)C_6H_2Br_2(C_2H_3O_2)\\ CN(C_2H_3O)C_6H_2Br_2(C_3H_3O_2)\end{matrix}\right.,$$

(m. p. 241°), showing that its constitution is—

$$C_6H_4\left\{\begin{matrix}CNH.C_6H_2Br_2.OH\\ CNH.C_6H_2Br_2.OH\end{matrix}\right..$$

Nitrous acid acts on the tetrabromodi-imidophthaleïn, yielding a body having the composition, $C_6H_4\left\{\begin{matrix}CNHC_6H_2Br(NO_2).OH\\ CNHC_6H_2Br(NO_2).OH\end{matrix}\right.$, two atoms of bromine being replaced by the nitro-groups, as is the case in the action of nitric acid on tetrabromfluoresceïn. P. P. B.

Constitution of the Dioxybenzenes. By H. FISCHLI (*Deut. Chem. Ges. Ber.*, xi, 1461—1464).—Phosphorus pentachloride reacts upon guaiacol to produce a small quantity of an oil, volatile in a current of steam. This oil treated with nitric acid yields a nitro-compound, which, after washing with water and soda, may be crystallised from alcohol in fine needles. This nitro-compound is nitro-orthochloranisol. Its formula is $C_6H_3(NO_2)Cl(OCH_3)$, and it forms colourless, brittle, shining needles, insoluble in cold, but somewhat soluble in hot alcohol. It melts at 93—94°. This substance is identical with the nitro-product obtained by direct nitration of orthochloranisol, which latter body is prepared from orthochlorphenol (b.p. 175—176°) by heating it with methyl iodide and solution of potash in methyl alcohol. This affords evidence that guaiacol, and therefore pyrocatechin, is an ortho-derivative, and since hydroquinone belongs to the para-series, the position of resorcin as a meta-compound is confirmed.

P. P. B.

Nitro-derivatives of Hydroquinone. By R. NIETZKI (*Deut. Chem. Ges. Ber.*, xi, 1448—1450).—When diethylhydroquinone which had been already prepared by Rakowsky (*Fehling's Handworterbuch*, ii, 560), is dissolved in acetic acid, and the solution treated with nitric acid, a mixture of di- and tri-nitro derivatives is obtained. By using dilute acid, or a mixture of nitric and sulphuric acids, these products may be obtained separately, as shown by Habermann (*Ber.*, xi, 1034) to be the case with dimethylhydroquinone. Dinitro-diethylhydroquinone, $C_6H_2(NO_2)_2(OC_2H_5)_2$ forms citron-yellow plates melting at 172°, insoluble in water but soluble in alcohol. The trinitro-compound, $C_6H(NO_2)_3(OC_2H_5)_2$, crystallises from its alcoholic solutions in pale, straw coloured needles, melting at 183°, and becoming darker on exposure to the air. Trinitro-diethylhydroquinone when heated in sealed tubes with alcoholic ammonia, is resolved into a red compound, which crystallises from its glacial acetic acid solutions in cinnabar-red plates, having a blue reflection, and melting at 245°. This compound has the composition $C_8H_{10}N_4O_5$; its constitutional formula is probably $C_6H(NO_2)_2(NH_2)_2.OC_2H_5$, and it owes its formation to the ethoxyl group being replaced by NH_2, a reaction which Salkowsky has shown to be characteristic of the nitrated anisols: in this case a nitro-group has also been replaced by NH_2. Further examination of the bye-products supports this conclusion. This compound has neither acid nor basic properties; when it is boiled with potash, ammonia is set free and a dibasic acid is obtained. This substance crystallises from alcohol in golden-yellow needles, with a violet reflex; it melts at 143°, but decomposes at the same time. It is slightly soluble in water, easily in alcohol, ammonia, and alkalis. Its composition is $C_8H_8N_2O_7$, and its constitutional formula is $C_6H(NO_2)_2(HO)_2.OC_2H_5$. Its compounds containing the alkali metals are easily soluble: its barium salt forms difficultly soluble, orange-coloured needles. P. P. B.

Pentahalogen-compounds of Resorcin and Orcin. By H. Claasen (*Deut. Chem. Ges. Ber.*, xi, 1438—1443).—Attempts to prepare other quinone compounds from tribromoresorci- and orci-quinone, save the pentabrom-derivatives, have been without success. The author has, however, been able to show that in the pentachloro- and bromo-derivatives described by Stenhouse, two of the halogen atoms are less stable than the other three, thus supporting Liebermann's view of their constitution. Pentabromoresorcin heated with formic acid or with aldehyde yields bromine, hydrobromic acid, and tribromoresorcin; on treating with acetic anhydride, α-tribromodiacetyl resorcin, $C_6HBr_3(C_2H_3O_2)_2$, is formed, which crystallises from alcohol in white needles, melts at 108°, and is easily soluble in alcohol, ether, and chloroform, and tolerably so in hot water.

Pentabromorcin yields similar results, viz., with formic acid, tribromorcin, $C_7H_3Br_3(OH)_2$, and with acetic anhydride, tribromo-diacetylorcin, $C_7H_3Br_3(C_2H_3O_2)_2$.

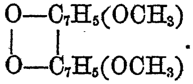
Pentabromoresorcin heated with sulphuric acid yields tetrabromoresorcin, $C_6Br_4(OH)_2$. The formation of this compound is apparently due to secondary reaction brought about by the liberated bromine, a supposition supported by the fact that some tribromoresorcin occurs in the mother-liquors. Tetrabromoresorcin melts at 163°, is easily soluble in hot alcohol, ether, and chloroform, with difficulty in water; it crystallises in small needles. Heated with acetic anhydride, it yields a diacetyl compound, $C_6Br_4(C_2H_3O_2)_2$, which melts at 169°, and is insoluble in water, but soluble in hot alcohol and ether.

Pentachlororesorcin is more stable than the bromo-compound, formic acid and aldehyde having no action on it; with a concentrated solution of potassium-hydrogen sulphite a violent reaction takes place, even in the cold, trichlororesorcin being formed. This compound, $C_6HCl_3(OH)_2$, crystallises in white needles, is easily soluble in alcohol, ether, and hot water, and melts at 69°.

The action of bromine on diacetylresorcin was investigated, in order to test whether a penta-compound was formed. This reaction resulted in the formation of tribromacetyl-resorcin, $C_6HBr_3(OH)(C_2H_3O_2)$; showing that only three hydrogen atoms are replaced by bromine, whilst an acetyl group is simultaneously removed by the hydrobromic acid.

When resorcin is added to an aqueous solution of potassic iodate, and then treated with a solution of iodine and potassic iodide, a brown flocculent precipitate separates out; from which by crystallising from carbon bisulphide, a compound is obtained in steel-grey needles: it loses iodine easily and appears to be a mixture of tri- and penta-iodoresorcin. When the alcoholic solution of this body is treated with potassium hydrogen sulphite, a colourless solution is obtained in which water produces a white flocculent precipitate of tri-iodoresorcin. Tri-iodoresorcin, $C_6HI_3(OH)_2$ melts at 154°, is easily soluble in alcohol, carbon bisulphide, and ether, difficultly soluble in hot water; it separates from these solutions in brown needles. It is easily dissolved by alkalis. Its alcoholic solution gives with alcoholic ammonia a brown crystalline precipitate, which is very unstable. With acetic anhydride, it yields a diacetyl compound, $C_6HI_3(C_2H_3O_2)_2$, which crystallises in needles and melts at 170°. P. P. B.

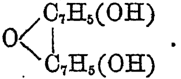
Derivatives of Hydrotoluquinone. By R. NIETZKI (*Deut. Chem. Ges. Ber.*, xi, 1278—1283).—The diacetyl derivative prepared by heating together acetyl chloride and hydrotoluquinone, crystallises from alcohol in large, colourless tables, melting at 52°. Oxidising agents resolve it easily into acetic acid and toluquinone. The dimethyl ether of toluquinone is prepared by heating at 100° under pressure hydrotoluquinone, methyl iodide, methyl alcohol, and caustic soda, or better, sodium methylate for 12 hours. The product which is freed from the monomethyl ether by means of potash, yields the dimethyl ether as a colourless liquid boiling at 214—218°, having a fennel-like odour. The solution of this ether in dilute acetic acid, when oxidised by a mixture of equal parts of sulphuric acid and potassium dichromate, yields a substance crystallising in pale brown needles. When the solution of this body in glacial acetic acid is diluted with water, it separates in bright red needles, but on crystallising slowly from alcohol, it separates in long, hair-like needles, which are slightly coloured; these in large quantities in the solution appear black, and when dried they have a silver-grey colour. Both varieties melt at 153° (uncorr.). It is insoluble in water, but dissolves in alcohol, ether, glacial acetic acid, and benzene, producing yellow solutions. The composition of this body is $C_{16}H_{16}O_4$, its formation being analogous to that of cedriret from the ether of pyrogalol (Hofmann, *Ber.*, xi, 329 and 797), and the author attributes to it the constitution—



$$\begin{array}{l} O—C_7H_5(OCH_3) \\ |\quad\ | \\ O—C_7H_5(OCH_3) \end{array}.$$

This body treated with aqueous solution of ammonium sulphide yields a hydroquinone which crystallises from benzene in slender, colourless needles, melting at 173°, and having the composition $C_{16}H_{18}O_4$. It is insoluble in water; its alcoholic solution becomes red on exposure to air.

Heated for several hours with concentrated hydrochloric acid in sealed tubes at 190°, it yielded methyl chloride and a crystalline mass, from which colourless shining plates were obtained by crystallisation from benzene and dilute alcohol. These lose water at 100°, and melt at 282°, but sublime below the melting point. Analysis shows its composition to be $C_{14}H_{12}O_3$, not $C_{14}H_{14}O_4$, as would be expected, and therefore points to the constitution,



$$O\Big\langle\begin{array}{l} C_7H_5(OH) \\ | \\ C_7H_5(OH) \end{array}.$$

The crystallised substance, however, loses 1 mol. of water on drying, so that its composition would be $C_{14}H_{14}O_4$. The author is not certain that this body is the required tetra-oxyditolyl, and that the molecule of water is only a molecule of water of crystallisation.

The monomethyl ether of hydrotoluquinone, which is obtained as a bye-product in the preparation of the dimethyl ether, is an oily liquid boiling at 240—245°, but when cooled it yields crystals melting at 72°, and on oxidation is converted directly into toluquinone with elimination of the methyl group. P. P. B.

Bromorosoquinone. By A. BAEYER and C. SCHRAUBE (*Deut. Chem. Ges. Ber.*, xi, 1301—1302).—This body is prepared by the oxidation of phenyl-tetrabromphthaleïn, dissolved in sulphuric acid, by means of nitric or chromic acid; and is probably a quinone of tetrabromodiphenyl similar to the body prepared by Kämmerer and Benzniger by the action of iodine on phenol in alkaline solution (*Ber.*, xi, 755).

Bromorosoquinone crystallises in beautiful red crystals, which appear of a steel-blue by reflected light; it dissolves in concentrated sulphuric acid with a violet colour, but is insoluble in other solvents. Alcoholic potash, or alcoholic solution of sulphurous acid or acid sulphite of potash converts the coloured bromorosoquinone into a colourless hydroquinone, which is easily reconverted into the quinone. The hydroquinone melts at 264°, and sublimes at higher temperatures, at the same time decomposing slightly; it is soluble in alkalis. In the oxidation of tetrabromphthaleïn, phthalic acid is also produced. P. P. B.

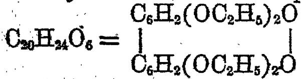
Ethyl Ethers of Pyrogallol, and the Cedriret of the Ethyl Series. By A. W. HOFMANN (*Deut. Chem. Ges. Ber.*, xi, 797—802).—In a previous paper (*Ber.*, xi, 329) the author has shown that the substance named *cedriret* or *coeruliguone* is a derivative of dimethyl-pyrogallic ether. He has now prepared a similar derivative from the diethyl ether of pyrogallol, and also made a complete examination of the three pyrogallic ethers. For their preparation he recommends a modification of the process already described by Benedikt (*Ber.*, ix, 125). Pyrogallol, in quantities of thirty grams, is heated with 3 mols. of caustic potash, 3 mols. of potassium ethyl sulphate, and a large excess of absolute alcohol, in soda-water bottles at 100° for 25—30 hours. The three ethers are simultaneously formed. To isolate them, the alcoholic liquid is saturated with hydrochloric acid gas, the alcohol removed by evaporation on the water-bath, and the dry residue exhausted with ether. The oil left when the ether is evaporated is washed with water to remove unchanged pyrogallol. It is then treated with a quantity of soda-solution far from sufficient to saturate it, which dissolves only the primary ether. A second treatment with soda in excess, dissolves the secondary ether, and from the alkaline mixture, the tertiary ether is washed out with common ether.

Monethyl Pyrogallate, $C_6H_3(OC_2H_5)(OH)_2$, is precipitated from its alkaline solution by hydrochloric acid as an oil, which after being distilled solidifies completely. The solid is crystallised repeatedly from dilute alcohol, and the ether is finally obtained in beautiful white stellate groups of needles, which melt at 95°. It is moderately soluble in cold, easily in hot, water, and mixes in all proportions with alcohol and ether. It reacts with ferric chloride like pyrogallol, and in alkaline solution is blackened by exposure to air. Oxidising agents attack it violently, but the products are ill-defined.

Diethyl Pyrogallate, $C_6H_3(OC_2H_5)_2OH$, is separated from the second alkaline solution above mentioned by saturating it with hydrochloric acid and agitating with ether. The residue from this solution is crystallised from dilute alcohol several times to remove primary ether. It melts at 79°. It much resembles the primary compound, but forms with soda a crystalline compound, which is not blackened by exposure to air. It yields a well-defined oxidation product, the cedriret mentioned below.

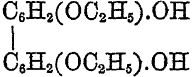
Triethyl Pyrogallate, $C_6H_3(OC_2H_5)_3$, is extracted from the oil left on evaporation of its crude ethereal solution, by collecting that portion of it which distils over at 250°. On adding water to an alcoholic solution of the fibrous crystalline mass thus obtained, until it becomes turbid, and cooling it in a freezing mixture, the ether is deposited in colourless needles. A second body, not as yet examined, remains in the mother-liquor. The crystals melt at 39°, and are not blackened by contact with air and alkalis. By oxidising agents the ether is converted into well crystallised products, not yet investigated.

Ethyl-cedriret, or more properly the cedriret of the ethyl series,



$$C_{20}H_{24}O_6 = \begin{array}{c} C_6H_2(OC_2H_5)_2O \\ | \qquad\qquad\qquad | \\ C_6H_2(OC_2H_5)_2O \end{array},$$

is obtained by oxidation from pyrogallol diethyl ether in the same way that ordinary cedriret is obtained from the dimethyl ether (*Ber.*, xi, 335). The best process consists in treating an acetic acid solution of the ether with potassic dichromate. From this mixture, it separates slowly in large well-formed prisms, which appear of a pure carmine-red colour by transmitted light, but by reflected light show the gold-green of cantharides with a tinge of blue. It is insoluble in water and ether, but soluble in alcohol. By rubbing or drying on the water-bath, it takes a bright red colour. Concentrated sulphuric acid forms with it a magnificent blue solution.



$$\begin{array}{l} C_6H_2(OC_2H_5).OH \\ | \\ C_6H_2(OC_2H_5).OH \end{array}$$

Hydro-ethylcedriret, $C_{20}H_{26}O_6$ = , is best obtained by treating an alcoholic solution of ethyl-cedriret with a stream, or a strong solution, of sulphurous acid gas. The liquid is quickly decolorised, and long snow-white silky needles of the hydro-compound separate. These melt, with decomposition, at 176°. The body is easily soluble in ether, but not in water. When dry it is stable, but when moist it turns red on exposure to air. The feeblest oxidising agents reconvert it into ethyl-cedriret. Ch. B.

Colouring Matters from Pyrogallic Ethers. By A. W. HOFMANN (*Deut. Chem. Ges. Ber.*, xi, 1455—1461).—Chloroform and carbon tetrachloride yield, when treated with the secondary ethers of pyrogallol, compounds analogous to those formed with phenol; if the reaction takes place in presence of alkalis, blue colouring matters are formed. The formation of these bodies is attended with most favourable results when dimethyl pyrogallate, treated with sufficient alcoholic potash or soda to form a salt, is heated with perchlorethane, C_2Cl_6, at 120—130° for some hours; a blue compound is thus formed. After evaporating off the alcohol, the blue mass obtained is treated with water, the perchlorethane filtered off, and the filtrate treated with hydrochloric acid. The solution then assumes a light red tint, and if an excess of acid is used, it becomes carmine. Brownish-yellow needles separate from the solution on standing, which are filtered off, washed with water, then dissolved in boiling alcohol. The alcoholic solution, on cooling, is treated with twice its volume of ether, when a substance crystallising in long orange-yellow needles is obtained. It may be heated to 100° without change. At 200° it melts and partially decomposes, forming a blue sublimate. It is easily soluble in glacial acetic acid, and is reprecipitated from this solution by alcohol. It is a weak acid, forming blue coloured salts with the alkali-metals, which are soluble in water, and precipitated from their aqueous solutions by an excess of alkali or alkaline salt. It dissolves in sulphuric acid, forming a red solution, which on heating becomes blue; the red colour is restored on addition of water. The composition of this substance is expressed by the formula $C_{25}H_{26}O_9$, which, together with its properties, show it to be identical with a body obtained by Liebermann from pitacal, and styled by him *eupittone* (*Ber.*, ix, 354). Pitacal is a substance isolated from beechwood tar by Reichenbach (*Schweigg. Jour. f. Chem. und Phys.*, lxviii, 1), and lately investigated by Grätzel. The formation of this compound is analogous to that of rosolic acid from phenol and oxalic acid, and, starting from the dimethyl ether of pyrogallol, may be expressed thus—

$$3C_8H_{10}O_3 + CO_2 = C_{25}H_{26}O_3 + 2H_2O.$$

Eupittonic acid, as the author styles this compound, may be regarded as rosolic acid in which six atoms of hydrogen are replaced by six methoxyl groups, thus: $C_{19}H_8(OCH_3)_6O_3$. Attempts to replace the methyl groups by hydrogen, by heating with hydrochloric acid, have resulted in the formation of pyrogallol.

If a solution of eupittonic acid in alcoholic ammonia be heated in sealed tubes at 160—170°, a blue solution is formed, from which, on cooling, broad colourless needles separate out. These are the crystals of a base which forms with acids yellowish-red solutions, becoming blue on evaporation. Its acetate is highly tinctorial, dyeing silk and wool directly like the aniline colours. The base may be precipitated from its salts by means of ammonia, separating out in nearly colourless crystals, which, however, become blue on exposure to the air. Heated to 100° this base undergoes no change, but at 200° it decomposes, ammonia being liberated. Its composition is expressed by the formula—

$$C_{25}H_{31}N_3O_9 \text{ or } C_{19}H_{11}(OCH_3)_6N_3.H_2O\ ;$$

and its formation may be expressed as follows:—

$$C_{25}H_{26}O_9 + 3NH_3 = C_{25}H_{29}N_3O_6.H_2O + 2H_2O.$$

The properties of this base recall those of rosaniline, and, like the latter, it crystallises with one molecule of water of crystallisation.

P. P. B.

Corallin and its Components. By K. Zulkowsky (*Deut. Chem. Ges. Ber.*, xi, 1426—1431).—The author, finding that the results of his experiments on this body do not agree with those of Gukassianz (*Ber.*, xi, 1179), has been led to publish the following. Corallin, prepared in whatever manner, is a mixture of several bodies belonging to two groups: 1, consisting of crystallisable bodies, such as aurin, which owe their existence to the action of nascent carbonic anhydride—

$$3C_6H_6O + CO_2 = \overset{\text{(Aurin.)}}{C_{19}H_{14}O_3} + 2H_2O,$$

and 2, a mixture of two amorphous bodies forming about 80 per cent. of the product, and resulting from the action of nascent carbon monoxide. One of these amorphous compounds is a resinous body, is not a pigment, and has been already described by the author as pseudorosolic acid (*Ber.*, x, 469). The second amorphous body, which has tinctorial properties, is styled corallin-phthaleïn, $C_{20}H_{14}O_4$. On treatment with bromine in glacial acetic acid solution, and addition of water, a bright red amorphous precipitate of a tetrabromo-product, $C_{20}H_{10}Br_4O_4$, is obtained. When dissolved in concentrated nitric acid and the solution diluted with water, a yellow amorphous tetranitro-product—

$$C_{20}H_{10}O_4(NO_2)_4,$$

separates out. It dyes wool yellow, like picric acid.

Accepting $C_{20}H_{14}O_4$, as the formula for corallin-phthaleïn, then the formula of the resinous product (pseudorosolic acid) may be either $C_{20}H_{16}O_4$ or $C_{20}H_{14}O_3$. Baeyer (*Ber.*, ix, 1230) has described two such bodies, the former as phenol-phthaleïn, the latter as phenol-phthalidin;

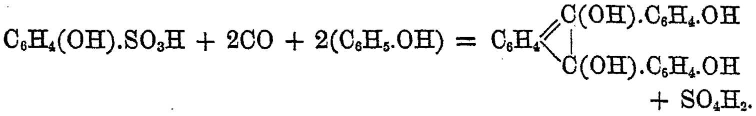
they yield isomeric bodies on oxidation. The evidence afforded by the analytical results, although not decisive, is in favour of the formula $C_{20}H_{16}O_4$; its formation would therefore be expressed as follows:—

$$3C_6H_6O + 2CO = C_{20}H_{16}O_4 + H_2O.$$

Corallin-phthaleïn dyes wool or silk yellow only when mordanted. With ammonia, it forms a red compound, and with aniline a blue one, both of which are purified with difficulty. It does not form an acetyl compound with acetic anhydride; it would, therefore, appear to be a quinone, $C_{20}H_{14}O_2(O_2)''$.

When the resinous product (pseudorosolic acid) is treated with acetic anhydride, it yields a diacetyl-compound as a white amorphous body melting at 100°, and having the composition $C_{20}H_{14}O_4(C_2H_3O_2)_2$. The composition of this diacetyl compound would tend to show that the original compound had the formula $C_{20}H_{14}O_3$. The author believes the formula to be $C_{20}H_{16}O_4$, and that acetic anhydride resolves it into $C_{20}H_{14}O_3$ and H_2O, a supposition supported by a similar observation of Baeyer's (*Ber.*, ix, 1234).

The formation of corallin-phthaleïn is explained as follows:—



$$C_6H_4(OH).SO_3H + 2CO + 2(C_6H_5.OH) = C_6H_4\left\langle\begin{array}{l}C(OH).C_6H_4.OH\\ |\\ C(OH).C_6H_4.OH\end{array}\right. + SO_4H_2.$$

It belongs to the para-series, since when sulphuric acid acts upon phenol at high temperatures, parasulphophenol is always formed.

The author confirms the observation of Gukassianz that the oxalic acid used to prepare these bodies is decomposed into CO and CO_2; the author has also observed that some formic acid is produced.

P. P. B.

Formation of Dyes by the Action of Benzoyl Trichloride on Phenols and Tertiary Aromatic Bases. By O. DOEBNER (*Deut. Chem. Ges. Ber.*, xi, 1236—1240).—Benzoyl chloride acting on a phenol produces a benzoic ether, but if a substance capable of abstracting water be present, such as zinc chloride, a large amount of colouring matter is likewise produced. The dye is also produced on the large scale by heating 2 mols. dimethylaniline, mixed with half its weight of zinc chloride, with 1 mol. benzoyl trichloride; a deep green mass is thus produced, which may be freed from excess of the original substances by steam. This product, known as *malachite green*, is a double zinc salt, and is soluble in water and alcohol. The free base is a red-brown uncrystallisable oil, whose salts are changed by an excess of mineral acid from a green to a yellow colour. The base has the constitution $C_{23}H_{24}N_2$, and is produced according to the equation—

$$\underset{\substack{\text{Benzoyltri-}\\\text{chloride.}}}{C_7H_5Cl_3} + \underset{\substack{\text{Dimethyl-}\\\text{aniline.}}}{2C_8H_{11}N} = C_{23}H_{24}N_2 + 3HCl.$$

Nascent hydrogen reduces this substance, forming a colourless solid tetramethyl-diamido-triphenylmethane, melting at 97—98°, and having the formula $C_{23}H_{26}N_2$. This compound therefore appears to be identical with that obtained by O. Fischer (*Ber.*, x, 1624, and xi, 950) from oil of bitter almonds and dimethylaniline, and from benzyl chloride and dimethylaniline. E. W. P.

Pinacones and Pinacolins. By W. THÖRNER and T. ZINCKE (*Deut. Chem. Ges. Ber.*, xi, 1396—1399).—The authors find that the α-benzopinacolin, already described by them (*Ber.*, xi, 68), is a mixture of the α- and β-modifications. When an alcoholic solution of benzophenone is treated with zinc and sulphuric acid, the product is a mixture of the α-pinacolin and pinacone, but the latter may be removed by heating it to a temperature of 190—200°, whereby it is resolved into benzhydrol and benzophenone, which are removed by ligroïn, and the residual α-pinacolin crystallised from alcohol. Thus prepared, α-pinacolin, $C_{26}H_{20}O$, crystallises in tufts of needles which melt at 204—204·5°; it dissolves sparingly in cold alcohol and glacial acetic acid, more easily when heated. Benzene, chloroform, &c., dissolve it easily; ether, however, only slightly. When α-benzopinacolin is heated with acetyl chloride, aqueous hydrochloric acid, or alcohol and sulphuric acid, it passes into the β-modification; oxidised by a solution of chromic anhydride in acetic acid, it is resolved into benzophenone and benzoic acid.

Behr (*Ber.*, v, 277) obtained a tetraphenyl-ethylene oxide by the oxidation of tetraphenyl-ethylene, which the authors find to be identical with α-benzopinacolin. This method of preparation is not conclusive as to the constitution of this latter body, and does not determine whether it is an inner anhydride or an ether of benzophenone; nor are the products obtained on heating α-benzopinacolin with soda-lime more conclusive as to its constitution. The chief product is a hydrocarbon mixed with some benzophenone and benzoic acid. This hydrocarbon has the empirical formula $C_{13}H_{10}$, and crystallises from hot alcohol or glacial acetic acid in well formed colourless crystals, which melt at 243—244°, and at the same time turn yellow. Benzene, toluene, carbon bisulphide, and chloroform dissolve it easily, whilst it is less easily soluble in ether, ligroïn, cold alcohol, or glacial acetic acid. Its solutions show a beautiful blue fluorescence, which is destroyed by picric acid. It is evident from the properties of this hydrocarbon that it is not identical with tetraphenyl-ethylene, of which, however, it may be a polymeride. The determination of its molecular formula will throw considerable light on the question of the constitution of α-benzopinacolin.

In preparing α-benzopinacolin the authors have observed that when the pinacone is resolved by heat into benzhydrol and benzophenone, water is formed. The formation of water is explained by the following reaction:—

$$C_{13}H_{12}O + C_{13}H_{10}O - H_2O = C_{26}H_{20}O.$$

The body having the composition $C_{26}H_{20}O$ is an isomeride of the α-pinacolin, crystallises in beautiful colourless crystals melting at 107—108°, and is identical with the substance which Linnemann obtained by heating benzhydrol, and described as an ether of benzhydrol. To it Linnemann attributes the constitution—

$$(C_6H_5)_2CH.O.CH(C_6H_5)_2.$$

The authors' observation that this substance, like α-benzopinacolin, may be converted into the β-modification, and that it is formed more easily by heating pinacone than benzhydrol, which itself is at first resolved into diphenylmethane and benzophenone, as follows:—

$$2C_{13}H_{12}O = C_{13}H_{12} + C_{13}H_{10}O + H_2O,$$

appears to show that this body is not an ether of benzhydrol, but is more nearly related to α-pinacolin. P. P. B.

On Oxyquinones and Resorcin Derivatives. By T. Diehl and V. Merz (*Deut. Chem. Ges. Ber.*, xi, 1229).—Amidodiimidoresorcin, heated at 170° with dilute hydrochloric acid, yields trioxyquinone, $C_6H_4O_5$. Corresponding trioxy-compounds may be obtained from other oxyquinones.

Diacetyl-resorcin is not convertible into tetranitro-resorcin, but yields, together with unaltered styphnic acid, a colourless, crystalline, acid substance. This body appears to belong to the fatty acid series.

E. W. P.

Oxytoluic Aldehydes from the three Isomeric Cresols, and the corresponding Oxytoluic Acids. By F. Tiemann and C. Schotten (*Deut. Chem. Ges. Ber.*, xi, 767—784).—The authors commence with a brief historical sketch of the cresols. For the preparation of para- and ortho-cresols, they recommend Meyer and Ambühl's method (*Ber.*, viii, 1074), which consists in heating aqueous toluidine sulphate with potassium nitrite; for preparing metacresol, they prefer Engelhardt and Latschinoff's method, viz., heating thymol with phosphorus pentoxide. The details of preparation and purification are given in each case.

From each of these three cresols, oxytoluic aldehydes may be obtained by the same process, as follows:—In a flask with inverted condenser, 20 pts. of the cresol are heated with a solution of 50 pts. of soda in 150 pts. water, and 30—40 pts. of chloroform are gradually added. The reaction is expressed by the equation—

$$C_7H_8O + 4NaHO + CHCl_3 = C_7H_6(NaO).COH + 3NaCl + 3H_2O.$$

The mixture usually becomes cherry-red, and when the reaction is over, it is acidified and distilled in a current of steam. The aldehyde homologous with salicylic aldehyde then distils over, together with unaltered cresol. The remaining liquid, filtered from a resinous (rosolic acid) compound, deposits on cooling crystals of a homologue of paraoxybenzoic aldehyde, when orthocresol or metacresol has been used, but not when paracresol has been employed. This fact confirms the authors' theory, that in the chloroform reaction the aldehyde group, COH, only enters into the ortho- and para-positions (referred to the hydroxyl groups). The homoparaoxybenzaldehydes from ortho- and meta-cresol easily give soluble compounds with sodium-hydrogen sulphite. The three homosalicylic aldehydes give sparingly soluble compounds with it.

In the names of these compounds the first prefix, ortho, &c. (standing before "homo"), refers to the CH_3 group, and indicates the cresol from which the aldehyde or acid has been prepared. Ortho-, meta-, or para-, coming after "homo," indicates the position of the COH group. The OH group is regarded as fixed.

By the above process the following compounds have been obtained from orthocresol:—

Orthohomosalicylic aldehyde, $C_6H_3(OH)(CH_3)(COH) = (1:2:6)$, melting at 170° to an oil which boils at 208—209°; and

Orthohomoparaoxybenzaldehyde, $C_6H_3(OH)(CH_3)(COH) = (1:2:4)$, crystallising from water in long feathery prisms which melt at 115°.

From metracresol have been prepared—

Metahomosalicylic aldehyde, $C_6H_3(OH)(CH_3)(COH) = (1:3:6)$, melting at 54°, boiling at 222—223°; and

Metahomoparaoxybenzaldehyde, $C_6H_3(OH)(CH_3)(COH) = (1:3:4)$, which crystallises from water in white tabular plates melting at 110°.

Paracresol gives only *one* aldehyde, namely:—

Parahomosalicylic aldehyde, $C_6H_3(OH)(CH_3)(COH) = (1:4:6)$, a bright yellow oil solidifying at 40°. When crystallised from dilute alcohol, this aldehyde melts at 56°, and boils at 217—218°.

The three homosalicylic aldehydes dissolve sparingly in water, easily in alcohol, ether, and chloroform. With ferric chloride, the ortho-aldehyde gives a bluish, the meta- a violet, and the para- a deep blue colour. Their odours resemble that of salicylic aldehyde. Like this, they are coloured yellow by alkalis, and their ammonia salts are sparingly soluble in excess of ammonia. Alcoholic solutions of these aldehydes, mixed with a little ammonia, give white precipitates with lead acetate and silver nitrate; with copper sulphate they give green precipitates which are not dissolved by excess of ammonia.

The two homoparaoxybenzaldehydes dissolve in hot water, easily in alcohol, ether, and chloroform. With ferric chloride the ortho-compound gives a bluish-violet, the meta-compound a bright rose-red colour. Their alkaline solutions are colourless. With metallic salts, they behave like the homologues of salicylic aldehyde, but their precipitates with cupric sulphate dissolve in excess of ammonia.

Oxytoluic aldehydes are oxidised with great difficulty when dissolved in water. The acetyl derivative of parahomosalicylic aldehyde, however, like the similar derivatives of salicylic and paraoxybenzoic aldehydes, may be oxidised with permanganate solution in presence of acetic acid. The corresponding acids are most simply formed when the aldehydes are introduced into fused potash containing a little water. The fusion is maintained for a few minutes, water added, and the acids precipitated with hydrochloric acid.

In this way are derived from orthocresol—

Orthohomosalicylic acid, $C_6H_3(OH)(CH_3)(COOH) = (1:2:6)$, melting at 159—160°, identical with *β-cresotic acid*, obtained in an impure state by Engelhardt and Latschinoff from impure orthocresol, by Kolbe and Lautemann's process; and in a pure form by Kekulé, from orthocresol by the action of carbonic acid and sodium (*Ber.*, vii, 1006); and by Ihle, from orthocresol, by Kolbe's process (*J. pr. Chem.*, xiv, 456); also

Orthohomoparaoxybenzoic acid, $C_6H_3(OH)(CH_3)(COOH) = (1:2:4)$, which crystallises from water in pale flesh-coloured needles containing ½ mol. of water of crystallisation. The acid dissolves sparingly in cold chloroform, rather more in boiling chloroform and cold water, easily in boiling water, alcohol, or ether. Heated to 100° it becomes anhydrous, and then melts at 172—173°.

From metacresol are derived—

Metahomosalicylic acid, $C_6H_3(OH)(CH_3)(COOH) = (1:3:6)$, melting at 173°, identical with γ-cresotic acid, prepared by Engelhardt and Latschinoff, by Kolbe and Lautemann's process, from metacresol (*Zeitschr. f. Chem.*, 1869, 622); and

Metahomoparaoxybenzoic acid, $C_6H_3(OH)(CH_3)(COOH) = (1:3:4)$, which crystallises from water in white needles, containing ½ mol. of water of crystallisation. This acid gives no colour-reaction with ferric chloride; when dry it melts at 177—180°.

Derived from paracresol we have—

Parahomosalicylic acid, $C_6H_3(OH)(CH_3)(COOH) = (1:4:6)$, identical with Engelhardt and Latschinoff's α-cresotic acid (*loc. cit.*), melting at 151°.

All these acids are scarcely distinguishable by their reactions, solubility, &c., from the acids with which they are homologous.

It will be seen that the four possible homologues of *meta*oxybenzoic acid are not produced by the chloroform reaction. One of these, in all probability orthohomometaoxybenzoic acid, has apparently been prepared by Flesch (*Ber.*, vi, 641), from camphor thiocymene, and Fittica (*Ber.*, vii, 927) has perhaps obtained another from cymene (parapropylmethylbenzene); but the statements of Jacobsen (*Ber.*, xi, 381 and 574) with regard to a third require confirmation.

The authors show by their own experiments, as well as by reference to those of other inquirers, that cresol from coal-tar is in reality a mixture of the three isomeric cresols. Ch. B.

Derivatives of Parahomosalicylic Aldehyde. By C. SCHOTTEN (*Deut. Chem. Ges. Ber.*, xi, 784—789).—This aldehyde is remarkable amongst the five isomerides obtained from cresol, for the ease with which it crystallises and enters into reactions.

By treating it, in quantities of a few grams, with excess of sodium-amalgam, for one or two days, neutralising *exactly* with sulphuric acid, and extracting with ether, *parahomosaligenin* (parahomosalicylic alcohol) $C_6H_3(OH)(CH_3)(CH_2OH) = (1:4:6)$ is obtained in colourless brilliant needles, melting at 105°, which are purified by crystallisation from a small quantity of hot water. The aldehyde dissolves easily in alcohol and ether, and in all proportions in boiling water. It reacts like saligenin.

Usually on neutralising with sulphuric acid a small quantity of a body precipitates, which melts at 200—205°, and is probably a homologue of saliretin.

When the aldehyde is boiled for five hours with methyl iodide, and a solution of potash in methyl alcohol, and the mixture poured into water, *methyl-parahomosalicylic aldehyde* separates as an oil, which, after washing with water and soda-solution, boils at 254°. It has an odour like creosote, and reacts neither with ferric chloride nor with caustic soda.

The potassium derivative of the aldehyde, when suspended in anhydrous ether and treated with acetic anhydride, gives a corresponding *acetyl* derivative, which melts at 57°, and is also unaffected by ferric chloride. It combines with hydrogen-sodium sulphite. It unites directly with one molecule of acetic anhydride, to form a compound from which the aldehyde character has entirely disappeared. This melts at 94°, and is completely decomposed by boiling water and by soda solution.

By boiling the aldehyde for an hour with an equal weight of dry sodic acetate and excess of acetic anhydride, the author has attempted to obtain homologues of coumarin and coumaric acid—

$$C_6H_3(CH_3)\left\{\begin{array}{l}\text{——O—CO} \\ \qquad\qquad\;\; | \\ \text{—}CH_7\text{═}CH\end{array}\right. \text{ and } C_6H_3(CH_3)\left\{\begin{array}{l}OH \\ CH\text{═}CH\text{—}COOH.\end{array}\right.$$

The product was poured into water, and the oil which separated taken up with ether. The ethereal solution was shaken, first with sodium hydrogen sulphite solution to remove unaltered aldehyde, and then with sodium carbonate, to remove acetocoumaric acid, which always forms in this reaction. On evaporating the remaining ethereal solution, a well crystallised product was obtained, which smelt of coumarin, and gave on analysis numbers which pointed to its being a mixture of methyl-coumarin and the addition-compound of acetoparahomosalicylic aldehyde with acetic anhydride mentioned above. It melted between 60° and 88°. The acid extracted from the ethereal solution by sodium carbonate, having been boiled with alkalis to remove the acetyl-group, gave an acid which melted at 185°, and showed the crystalline form and reactions of orthocoumaric acid. It was not analysed.

Parahomosalicylic aldehyde and orthohomoparaoxybenzaldehyde, on nitration, yield only orthonitro-derivatives, the first melting at 141°, the second at 152°. Both are crystalline bodies, insoluble in cold, soluble in hot water. The aldehyde character is preserved in both. Ordinary salicylic aldehyde, according to Mazzara (*Gazz. chim. ital.*, vi, 460), gives an ortho-nitro- and a para-nitro-derivative. But in the above oxytoluic aldehydes the "para" position is already occupied, in the first by a methyl group, and in the second by the group COH. These aldehydes, therefore, give only orthonitro-compounds.

Ch. B.

Oxidation of Cumic Acid with Potassium Permanganate. By R. Meyer (*Deut. Chem. Ges. Ber.*, xi, 1283—1287).—A solution of cumic acid in caustic soda, oxidised by potassium permanganate, yields a small quantity of terephthalic acid, and a new acid, the weight of which almost equals that of the cumic acid employed. This new acid is soluble in hot water, and crystallises from a concentrated aqueous solution in dendritic crystals, whilst from a dilute solution it crystallises in long, thin prisms. It is very soluble in alcohol and ether, and melts at 155—156°; it may be sublimed, but at the same time undergoes partial decomposition. From analysis its composition is $C_{10}H_{12}O_3$.

Its ammonium salt is soluble, and its neutral solution gives no reaction with ferric chloride. The copper salt is obtained, first as a bright blue amorphous precipitate, which on standing becomes crystalline. The lead salt is obtained as a white amorphous precipitate, which melts in boiling water. The silver-salt is a white crystalline body, not easily acted on by light; and may be crystallised from hot water in beautiful, shining, transparent, rhombic plates. Its analysis shows the acid to be monobasic. This new acid differs from cumic acid, inasmuch as an atom of hydrogen in the latter is replaced by a hydroxyl group; the fact that it yields terephthalic acid on oxidation with potassium dichromate and sulphuric acid shows that the hydroxyl group is not in the aromatic nucleus, but in the side chain, and the author, therefore, styles it *oxypropylbenzoic* acid. P. P. B.

Solubility of Salicylic and Benzoic Acids. By E. BOURGOIN (*Compt. rend.*, lxxxvii, 62—64).—The author finds for salicylic acid a higher degree of solubility in water than has been given by most authors, viz., that 1000 parts of water at 15° dissolve 2·25 parts, and at 100°, 79·25 parts. Curves of solubilities for salicylic, and also for benzoic acid are given in this paper; they cross one another at a temperature of 40°. Below that temperature salicylic acid is somewhat less soluble than benzoic acid, whilst above 40° it is more soluble.

R. R.

On a Dichlorsalicylic Acid, and on Monochlorsalicylic Acid (m. p. 172°). By E. J. SMITH (*Deut. Chem. Ges. Ber.*, xi, 1225).—By the action of chlorine on salicylic acid dissolved in acetic acid the author has not succeeded in preparing a dichlorinated acid (m. p. 224°) identical with that described by Rogers, but has obtained an acid melting at 214°, crystallising in dendritic flocks, and yielding no nitro-derivative; several of its salts and ethers which are solid are described. During the preparation of the dichlor-acid a monochlor-acid (m. p. 172°) is also formed, and this appears to be identical with that obtained by Hübner (*Ber.*, vi, 174); some of its salts and derivatives are described. E. W. P.

Addition of Hydrobromic Acid by means of a Solution of Hydrobromic Acid in Glacial Acetic Acid. By R. ANSCHÜTZ and L. KINNKULT (*Deut. Chem. Ges. Ber.*, xi, 1221).—A solution of hydrobromic acid in glacial acetic acid is found to be efficacious in introducing that acid into a compound; for example, cinnamic acid becomes monobromhydrocinnamic acid when heated in a closed tube for a short time on a water-bath with a saturated solution of hydrobromic acid in acetic acid. E. W. P.

Azobenzene-acetonecarbonic Acid. By J. ZÜBLIN (*Deut. Chem. Ges. Ber.*, xi, 1417—1420).—The study of this acid, prepared by

v. Meyer from ethyl acetonecarbonate and diazobenzene nitrate, and described under the name of azophenylaceto-acetic acid—

$$C_6H_5.N_2.CH(CO.CH_3).COOH,$$

but which the author proposes to style azobenzene-acetonecarbonic acid, has yielded the following results. Its salts are well characterised: the potassium compound is prepared by mixing an alcoholic solution of the acid with a similar solution of potash, and is obtained in yellow shining plates, having the composition $C_{10}H_9N_2O_3K$. The barium salt is obtained as a bright yellow precipitate, the lead salt in yellow flocks, the silver salt as a yellow curdy precipitate, $C_{10}H_9N_2O_3Ag$, and the copper salt as a yellow precipitate.

The ethyl salt of this acid is formed in the preparation of the acid itself, and is obtained by crystallisation from alcohol in hard vitreous honey-coloured crystals; when crystallised quickly, it forms a canary-coloured powder; it melts at 59·5°, and has the composition $C_{10}H_9N_2O_3.C_2H_5$. It is saponified very easily, and yields the acid, melting at 154—155°.

The formation of this acid must take place in two phases, viz.:—

$$\text{I. } C_4H_4KO_3.C_2H_5 + C_6H_5.N_2.NO_3 = KNO_3 + \underset{\text{Azobenzene-acetocarbonic ether.}}{C_6H_5.N_2.C_4H_4O_3.C_2H_5}$$

$$\text{II. } C_6H_5.N_2.C_4H_4O_3.C_2H_5 + KHO = C_2H_5.OH + C_6H_5.N_2.C_4H_4O_3K.$$

A portion also of the azobenzene-acetonecarbonic ether remains unacted upon. When azobenzene-acetonecarbonic acid is heated with hydrochloric acid in sealed tubes, or with alcoholic potash, it is destroyed, yielding resinous products. Reduced with tin and hydrochloric acid it yields a complicated oily base.

Para-azotolueneacetonecarbonic acid—

$$CH_3.C_6H_4.N_2.CH(CO.CH_3).COOH,$$

is prepared in a manner analogous to the benzene-compound, viz., from paradiazotoluene nitrate and ethyl acetonecarbonate. Crystallised from alcohol, it forms orange-yellow shining needles, melting at 180—190°. The ethyl ether is prepared in a manner similar to that of the benzene derivative; it occurs either as a yellow crystalline powder, or vitreous honey-coloured prisms; like the benzene derivative it saponifies easily. The salts resemble those of the benzene derivative.

P. P. B.

Reduction of Aldehydo-oxybenzoic Acids to Alcoholic Acids.

By C. L. Reimer (*Deut. Chem. Ges. Ber.*, xi, 790—793).—The aldehydo-acids prepared by the author and Tiemann from salicylic and paraoxybenzoic acids by the action of chloroform on their alkaline solutions, are converted by oxidation into dicarboxyl-derivatives of phenol. By treating them with sodium-amalgam, the author has now effected their reduction into *alcohol acids*. Bodies of this class, to which the *oxymethyl-phenylformic acid* of Kekulé and Dittmar (*Ber.*, iii, 894), and perhaps *meconin*, belong, have been hitherto but little studied. The process in each case was the following:—

1 part of the aldehydo-acid was suspended in about 10 parts of water, and treated gradually with 50 parts of 3 per cent. sodium amalgam. The reduction of the aldehyde under these circumstances was nearly complete, but resinous products were invariably formed at the same time. Hydrochloric acid was then added in slight excess, and the alcohol-acid, mixed with resin, extracted by agitation with ether. The separation of the resin was effected, either by dissolving the mixture in ammonia, adding barium chloride, and leaving the solution at rest for some weeks, when the resin separated completely in combination with barium; or by acidifying the ammoniacal solution with hydrochloric acid, quickly filtering off the resin mixed with some acid, and allowing the rest of the acid to separate spontaneously.

Paraoxymethyl-salicylic acid, $C_6H_3(OH)(COOH)(CH_2OH) = (1:2:4)$, from para-aldehydosalicylic acid, crystallises from ether in long prisms containing 1 mol. water of crystallisation. It is sparingly soluble in water, more so in alcohol and ether. It decomposes at 160°, and is resinised by warm mineral acids.

Permanganate solution converts this acid in the cold into α-oxyisophthalic acid; when heated with potassium dichromate it is oxidised to para-aldehydosalicylic acid.

Ortho-oxymethylsalicylic acid, $C_6H_3(OH)(COOH)(CH_2OH) = (1:2:6)$, is precipitated as an oil which solidifies to crystals melting at 142°. A solution of this acid in water, especially in presence of free mineral acid, is resinised by heat. An ammoniacal solution of it heated with potassic dichromate reproduces the corresponding aldehydo-acid.

Ortho-oxymethyloxydracylic acid (saligeninparacarbonsäure)—

$$C_6H_3(OH)(COOH)(CH_2OH) = (1:4:6),$$

obtained by reduction of ortho-aldehydo-oxydracylic acid, is much more stable than its isomerides, and does not melt at 270°. It is not coloured either by sulphuric acid or by ferric chloride. With the latter reagent its isomerides, mentioned above, give intense violet colours.

Ch. B.

Action of Chloroform on α- and β-Oxyisophthalic Acids in Alkaline Solution. By C. L. Reimer (*Deut. Chem. Ges. Ber.*, xi, 793—797).—By means of the chloroform reaction the author has succeeded in introducing aldehyde-groups into these acids. 1 part of acid and 1½ parts of potash were dissolved in 3 parts of water, and 1½ parts of chloroform gradually added to the mixture, kept boiling for five or six hours. The excess of chloroform having been expelled by evaporation, and the liquid supersaturated with hydrochloric acid, the aldehydes were extracted by agitation with ether. The ethereal solutions were then shaken with sodium-hydrogen sulphite solution, and the aldehydes again separated from the latter by boiling with sulphuric acid. They were purified by dissolving them in ammonia, adding ammonium chloride and magnesium sulphate, and leaving the liquid to itself for some days; sparingly soluble magnesian salts then separated, which were decomposed by heating with dilute hydrochloric acid.

Aldehydo-α-oxyisophthalic acid, $C_6H_2(OH)(COOH)(COOH)(COH) =$

(1 : 2 : 4 : 6), crystallises from water in white felted needles, which are slowly decomposed above 200°, and melt at 260° with decomposition. It is easily soluble in alcohol, ether, and hot water, sparingly in cold water. Its neutral solutions are colourless, those containing excess of alkali yellow, and both show green fluorescence. Calcium and magnesium salts do not precipitate its neutral solutions: barium salts do so only after the lapse of some time. Its basic salts are mostly insoluble. The acid silver salt dissolves in hot water.

The filtrate from the magnesium salt of this acid, obtained during the process of purifying it, gives with acids a precipitate of para-aldehydo-salicylic acid, evidently produced by reduction of the oxy-isophthalic acid, in the same way that paraoxybenzaldehyde is formed from paraoxybenzoic acid (*Ber.*, ix, 1267).

Aldehydo-β-oxyisophthalic acid, $C_6H_2.(OH)(COOH)(COOH)(COH)$ (1 : 2 : 6 : 4), crystallises in long slender needles containing ½ mol. of water of crystallisation. It melts at 237—238°. In crystalline form, fusing point, solubility, reaction with iron, and the blue fluorescence of its solutions, it differs but little from β-oxyisophthalic acid. Its alkaline solutions are colourless; its salts in general resemble those of its isomeride.

These aldehydo-acids cannot be oxidised by fusion with potash; but by careful treatment of their slightly alkaline solutions with potassium permanganate they both yield a tricarboxyl-phenol (phenoltricarbonsäure), which crystallises from water in small prisms melting at 270°. This body has most of the characters of *oxytrimesic acid* obtained synthetically by Ost from salicylic acid and carbonic acid. The author, however, was unable to make an analysis of it. Ch. B.

Identity of Usnic and Carbusnic Acids. By E. Paternò (*Gazzetta chimica italiana*, viii, 225—233).—Usnic acid was discovered in 1843, by Knop (*Liebig's Annalen*, xlix, 103), in several lichens of the genera *Usnea*, *Parmelia*, *Evernia*, *Cladonia*, and *Lecanora;* and, nearly at the same time, Rochleder A. Heldt (*ibid.*, xlviii, 12) observed the presence of the same acid in *Cladonia rangiferina* and *Usnea barbata* (Fries). Some years afterwards Stenhouse (*ibid.*, lviii, 97, 114) found usnic acid in *Evernia prunastri*, and obtained, by dry distillation of the crude acid, a new substance which he named *beta-orcin.* Hesse, in 1861 (*ibid.*, cxvii, 343), observed that the acid extracted from *Cladonia rangiferina* melted at 175°, and therefore regarded it as isomeric with Knop's usnic acid, distinguishing it as *beta-usnic acid;* and in 1866 the same chemist, in examining *Usnea barbata*, Hoffm., extracted from it a new yellow crystalline substance, deceptively like usnic acid in most of its properties, but differing from it slightly in composition, and melting at 195·4° (usnic acid at about 200°). This substance he designated as *carbusnic acid*, assigning to it the formula $C_{19}H_{16}O_8$, usnic acid being at that time generally regarded as $C_{18}H_{18}O_7$.

The existence of beta-usnic acid was corroborated in 1870 by Stenhouse, who, moreover, showed (correcting a former statement) that beta-orcin was a derivative, not of usnic acid, but of the acid extracted from *Cladonia rangiferina*, for which he proposed the name *cladonic* instead of beta-usnic acid.

The existence of the second acid (carbusnic) was supposed to be confirmed by the difference of the results obtained by Paternò and by Salkowski with the acids obtained from *Zeora sordida* and from *Usnea barbata*, Fr. (*florida*, Hoffm.), notwithstanding that the supposition of Salkowski's acid being carbusnic acid was to a certain extent in contradiction to his own analyses of the salts of this acid, which gave for it an equivalent number (molecular weight) between 329·7 and 347·1, whereas the formula $C_{19}H_{16}O_8$ requires 372.

Finally, Hesse in his last memoir has re-examined the acid prepared from *Usnea barbata*, Hoffm., with results confirmatory of those which he had previously obtained. He is still of opinion that the lichen just mentioned contains an acid having the composition $C_{19}H_{16}O_8$, mixed perhaps with a small quantity of usnic acid. This conclusion is based on the result of two combustions of the acid, which gave, as a mean, 61·72 p. c. C and 4·42 H (the formula $C_{19}H_{16}O_8$ requiring 61·29 and 4·30), and on analyses of the potassium salt. This salt crystallises from alcohol of 93 p. c. in yellow flattened prisms containing 4·09 p. c. water and 9·46 potassium, and from dilute alcohol in beautiful pale-yellow leaflets containing 11·18 water and 8·97 potassium. These results agree tolerably well with the formulæ, $C_{19}H_{15}KO_8 + H_2O$ (4·20 H_2O and 9·15 K), and $C_{19}H_{15}KO_8 + 3H_2O$ (11·63 H_2O and 8·47 K), and are regarded by Hesse as affording decided confirmation of the existence of carbusnic acid, $C_{19}H_{16}O_8$.

On the other hand, Paternò finds that usnic acid from *Zeora sordida*, from which he formerly prepared decarbusnein, pyrousnic acid, and other well-defined compounds, yields, when boiled with potassium bicarbonate in such quantity as to leave a little of the acid undissolved, a potassium salt which crystallises from water in a mass of yellow leaflets giving off 12·23 p. c. water at 110°; from alcohol of 93 p. c. in yellow prisms containing 4·32 p. c. water and 9·48 p. c. potassium (or 9·91 calculated on the dry salt); and from alcohol of 51 p. c. in pale yellow leaflets containing 12·19 p. c. water and 8·64 potassium (9·84 for the dry salt).

These results agree very nearly with those which Hesse obtained with the potassium salt of the acid prepared from *Usnea barbata* (Hoffm.), but they are more in accordance with the formula $C_{18}H_7KO_8$ for the dry salt, than with $C_{18}H_{15}KO_7$, which would correspond with $C_{18}H_{16}O_7$, the formula originally assigned by Paternò to usnic acid.

	$C_{18}H_7KO_8 + 3H_2O$.			$C_{18}H_7KO_8 + H_2O$.			
	Calc.	Exp.		Calc.	Exp.		
		Paternò.	Hesse.		Paternò.		Hesse.
Water	11·89	12·19	11·49	4·30	4·32	4·07	4·11
Potassium....	8·59	8·64	8·97	9·33	9·48	—	9·46

Anhydrous salt, $C_{18}H_7KO_8$.

	Calc.	Paternò.
Potassium	9·75	9·91 and 9·84

Knop also, in 1843, found in dried potassium usnate 9·16 p. c. potassium, which agrees better with $C_{18}H_{17}KO_8$ than with $C_{18}H_{15}KO_7$, the latter requiring 10·20 p. c. potassium.

On the other hand, the experiments of Paternò on the derivatives of the compound hitherto called usnic acid (extracted from *Usnea barbata* and *Zeora sordida*) have clearly shown that this compound has the composition $C_{18}H_{16}O_7$; and since this compound, when treated with alkalis, yields salts having the composition $C_{18}H_{16}M''O_7$, it must be inferred to be, not an acid, but an anhydride, a view which is confirmed by other facts and considerations. Thus the formation of decarbusneïn and pyrousnic acid from the compound $C_{18}H_{16}O_7$ may be represented by the equations—

$$C_{18}H_{16}O_7 + 2H_2O = CO_2 + C_2H_4O_2 + C_{15}H_{16}O_5.$$
$$C_{18}H_{16}O_7 + 3H_2O = CO_2 + C_2H_4O_2 + C_3H_6O + C_{12}H_{12}O_5.$$

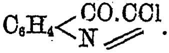
Here the elimination of CO_2 from the compound $C_{18}H_{16}O_7$ is accompanied by assumption of the elements of water, which would not be necessary if this compound were really an acid containing the group CO_2 in the form of CO.OH, as in the transformation of benzoic, salicylic, and orsellinic acids into benzene, phenol, orcin, &c.

The experiments above detailed are sufficient to establish the identity of Hesse's carbusnic acid from *Usnea barbata*, Hoffm., with usnic acid. The carbusnic acid which Salkowski obtained from *Usnea florida*, Hoffm., is also identical therewith, inasmuch as Paternò has found that when boiled with aniline it yields two compounds identical with those obtained from usnic acid, one melting at 142°, the other at 170°. The acid regenerated from these compounds by hydrochloric acid is converted by heating with alcohol in a sealed tube into decarbusneïn, $C_{15}H_{16}O_5$.

The so-called *usnetic acid*, $C_9H_{10}O_3$, recently found by Hesse in the mother-liquors of usnic acid from *Usnea barbata*, is regarded by Paternò as identical with decarbusneïn. H. W.

Synthesis of Isatin and Indigo-blue. By A. BAEYER (*Deut. Chem. Ges. Ber.*, xi, 1228).—Since oxindol is identical with orthoamidophenylacetic acid, $C_6H_4<\genfrac{}{}{0pt}{}{CH_2.CO}{NH\text{———}}|$, it follows that, if the replacement of the CH_2 group by CO is possible, the synthesis of isatin will be complete. This has been done by converting the NO group in nitroso-oxindol into the amido-group, and finally oxidising the amido-group.

From isatin, indigo-blue is obtained in the usual manner (*Ber.*, iii, 688). Researches, at present incomplete, tend to show that indigo-blue can also be obtained from amido-oxindol. E. W. P.

Synthesis of Indigo-blue. By A. BAEYER (*Deut. Chem. Ges. Ber.*, xi, 1296—1297).—The author points out that the production of indigo-blue from isatin by means of phosphorus trichloride, acetyl chloride, and phosphorus is not satisfactory, inasmuch as the product consists chiefly of indigo purpurin, and again, it is not quite clear how this mixture acts on isatin. Phosphorus pentachloride may, however, be used instead of this mixture; when heated with isatin, hydrochloric acid is set free, and a product obtained which probably has the composition  $C_6H_4<\begin{matrix}CO.CCl\\N\,/\!\!/\end{matrix}$. This isatin chloride may be reduced either by heating with phosphorus, or by treatment of its alcoholic solution with zinc-dust and acetic acid, whereby indigo is formed. The best reducing agent appears to be ammonium sulphide; all, however, yield an indigo mixed with more or less indigo-purpurin. P. P. B.

Indigo-blue from Polygonum tinctorium and other Plants. By E. SCHUNCK (*Chem. News*, xxxvii, 223).—From the dried leaves of the *Polygonum tinctorium*, a plant used by the Chinese for the manufacture of indigo, the author has obtained a substance which is identical in its properties with the *indican* of the common woad plant. His experiments show that the leaf-cells of the fresh leaves contain no ready-formed colouring matter, with the exception of chlorophyll, and that the indigo-blue is formed by the decomposition of *indican*, when the cell-vitality is destroyed by extreme cold, organic lesion, or chemical reagents.

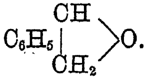
The leaves of *Bletia Tankervilliæ* and *Callanthi veratrifolia* also contain indican, and it is believed that this substance will be found in all cases to be the source whence indigo-blue is derived.

A substance having the properties of tyrosine was obtained from a long-standing alcoholic extract of dried woad leaves, and was probably produced from the indican by partial decomposition. A. J. C.

Cinnamene. By W. v. MILLER (*Deut. Chem. Ges. Ber.*, xi, 1450—1451).—The author points out, that not only do the different varieties of storax differ in the amount of cinnamene they yield, but also that the cinnamene itself varies in properties, *e.g.*, in its specific rotatory power. As a means of purifying cinnamene, use is made of the formation of a crystalline bromide. To prepare this compound, the cinnamene is dissolved in carbon bisulphide, and then treated with bromine; after evaporation of the bisulphide, the bromide separates out. This may be further purified by distillation in a current of steam. When crystallised from dilute alcohol it melts at 73°; its composition is expressed by the formula $C_8H_8Br_2$. A yellow oil distils over together with the bromide, and in the retort a dark yellow oil remains, which solidifies in a freezing mixture. The author does not intend continuing the study of these bodies, as Krakau (*Ber.*, xi, 1259) is also investigating this subject. P. P. B.

Styrolene Alcohol. By A. BREUER and T. ZINCKE (*Deut. Chem. Ges. Ber.*, xi, 1399—1403).—In a former communication the authors pointed out the possibility of obtaining from styrolene (cinnamene), $C_6H_5.CH{=}CH_2$, as from stilbene, $C_6H_5.CH{=}CH.C_6H_5$, two isomeric alcohols. The attempts made to prepare this alcohol from styrolene dibromide (m. p. 73·5—74°, and not 68—69°, as stated generally), have resulted in the formation of ordinary styrolene alcohol. When styrolene dibromide, silver benzoate, and toluene were heated together, it was observed, in one instance only, that a small quantity of a body was formed, which melted at 123—126°, and which, when heated with dilute sulphuric acid, gave the odour of pinacoline, thus showing it to be the desired alcohol.

Pinacolins of Styrolene alcohol. Styrolene alcohol, which has the two hydroxyl groups attached to neighbouring carbon atoms, belongs to the pinacones, and, when boiled with dilute sulphuric acid, is resolved, with loss of H_2O, into a pinacolin. The following formulæ show the constitution of the three possible pinacolins:—α,



$C_6H_5\left|\begin{array}{l}CH\\ CH_2\end{array}\right\rangle O.$

β, or phenylacetic aldehyde, $C_6H_5.CH_2.COH$. γ, or acetophenone, $C_6H_5.CO.CH_3$. When styrolene alcohol is warmed with sulphuric acid (20 p. c.), it is converted into the β-pinacolin, a liquid identical with Radzizewski's phenylacetaldehyde; when treated with alcoholic potash this yields benzoic acid, and by the action of sulphuric acid diluted with an equal volume of water, is converted into a hydrocarbon, $C_{16}H_{12}$. Styrolene alcohol treated with sulphuric acid diluted with 5 parts of water, yields the α-pinacolin, a viscid, slightly yellow liquid boiling at 260° under a pressure of 50 mm. It is converted into the β-modification by the action of dilute sulphuric acid, concentrated hydrochloric acid, acetyl chloride, and benzoyl chloride; it also, like the β-modification, yields the hydrocarbon $C_{16}H_{12}$. With phosphorus pentabromide, it yields styrolene bromide, $C_6H_5.CHBr.CH_2Br$, which is converted into styrolene dibenzoate by the action of benzoic acid. By oxidation with a glacial acetic acid solution of chromic acid, benzoic acid is formed, and also a small quantity of what appears to be phenylacetic acid.

These facts show that styrolene alcohol is analogous to the hydrobenzoïns, the β-pinacolin corresponding with the diphenylacetaldehyde, whilst the α-pinacolin corresponds with the hydrobenzoïn anhydrides. This, together with the difficulty with which α-pinacolin is converted into its ether, and its high boiling point, leads the authors to adopt the following constitutional formula for the α-pinacolin:—

$$CH(C_6H_5).O.CH(C_6H_5).CH_2.O.CH_2.$$

P. P. B.

Dioxybenzophenone. By A. BAEYER and J. B. BURKHARDT (*Deut. Chem. Ges. Ber.*, xi, 1299—1300).—When phenolphthaleïn is fused with potash, it is decomposed into benzoic acid and dioxybenzophenone, and not, as previously stated by the authors, into a hydrate of the phthaleïn (*Ber.*, ix, 1232). This decomposition is expressed as follows:—

$$C_6H_4\left\{\begin{array}{l}CO.C_6H_4.OH\\ CO.C_6H_4.OH\end{array}\right. + H_2O = C_6H_5.COOH + CO\left\{\begin{array}{l}C_6H_4.OH\\ C_6H_4.OH\end{array}\right.$$

The dioxybenzophenone melts at 206°, and can be distilled without decomposition; its aqueous solution is not coloured by ferric chloride: with acetic anhydride it forms a diacetyl-compound melting at 148°. The properties of this body make it probable that it is identical with the dioxybenzophenone prepared by Gail from dioxydiphenylmethane (*Ber.* xi, 746; p. 671 of this volume).

Dioxybenzophenone, when fused with potash, is resolved into carbonic acid and phenol; with bromine it yields a tetrabromo substitution product melting at 213—214°, and finally, when distilled with soda solution and zinc-dust, it yields what appears to be a dioxybenzhydrol.

P. P. B.

Dioxybenzophenone from Rosaniline. By C. LIEBERMANN (*Deut. Chem. Ges. Ber.*, xi, 1434—1438).—Caro and Graebe (*Ber.*, xi, 1222 and 1116) find that when aurin and water are exposed to a high temperature, dioxybenzophenone is formed, identical with that prepared by Städel and Gail (this vol. p. 671). They also express the opinion that the product obtained by the author (*Ber.*, vi, 951) by the action of water on rosaniline hydrochloride, is either dioxybenzophenone or a mixture of it with higher homologues. The study of this compound confirms the first supposition, the author finding it to agree in all its properties with dioxybenzophenone. A repetition of the reaction with aurin and with pararosaniline shows that they both yield dioxybenzophenone. Its formation from rosaniline and pararosaniline is explained as follows:—

$$C_{20}H_{19}N_3 + 4H_2O = 3NH_3 + \underset{\text{Cresol.}}{C_7H_8O} + \underset{\substack{\text{Dioxybenzo-}\\\text{phenone.}}}{C_{13}H_{10}O_3.}$$

In the hope to obtain aurin, the author has heated paraoxybenzaldehyde with oxalic acid and sulphuric acid: a red colouring-matter is formed, as observed by Reimer and Tiemann, which, however, analysis shows to be neither aurin nor rosolic acid.

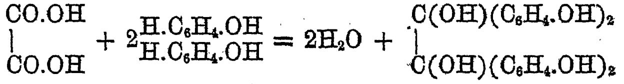
This colouring-matter the author thinks may belong to the group of aldehyde-phenol condensation-products investigated by Baeyer (*Ber.*, v, 280). Its formation may be explained by the following equation:—

$$2C_7H_6O_2 + 2C_6H_6O + O = C_{22}H_{22}O_6 + H_2O.$$

Supposing its constitution to be

$$(C_6H_4OH)_2C(OH).C(OH)(C_6H_4.OH)_2,$$

then this would be resolved by sulphuric acid into a compound resembling the pinacones. This compound the author thinks is the chief product of the action of phenol on oxalic and sulphuric acids, the reaction being expressed as follows:—



$$\begin{array}{l}CO.OH\\ |\\ CO.OH\end{array} + 2\begin{array}{l}H.C_6H_4.OH\\ H.C_6H_4.OH\end{array} = 2H_2O + \begin{array}{l}C(OH)(C_6H_4.OH)_2\\ |\\ C(OH)(C_6H_4.OH)_2\end{array}$$

P. P. B.

On Naphthalene Chloride. By A. ATTERBERG (*Deut. Chem. Ges. Ber.*, xi, 1223).—The author having acted on naphthalene with chlorine without obtaining β-naphthalene tetrachloride according to the statements of E. Fischer (*Ber.*, xi, 735), doubts the existence of that body, not only because he himself has not obtained it, but also because the melting point is not constant (176—180°). E. W. P.

Chlorine-compounds of Naphthalene. By E. FISCHER (*Deut. Chem. Ges. Ber.*, xi, 1411—1412).—This is a defence of the author's work against the criticisms (*Ber.*, xi, 735) of Atterberg. The final settlement of the question raised, viz., the constitution of the compound styled by the author β-naphthalene tetrachloride, is to be looked for in a repetition of the work, to be shortly undertaken by the author.

P. P. B.

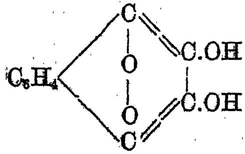
Derivatives of α-Naphthaquinone. By T. DIEHL and V. MERZ (*Deut. Chem. Ges. Ber.*, xi, 1314—1324).—In the preparation of naphthalic acid, which was the starting point in this research, the authors used α-dinitronaphthol (Martius's yellow), which is converted into diimidonaphthol, and then boiled with solution of carbonate of soda. By this method a better yield is obtained than when it is prepared by the method of Graebe and Ludwig (*Annalen*, cciv, 331). Naphthalic acid, after several crystallisations and sublimations, melts at 179°. Diamidonaphthol, heated at 188° with dilute hydrochloric acid, and exposed to the air, also yields naphthalic acid. When diamidonaphthol is heated with sulphuric acid and potassium dichromate, the chromate of diimidonaphthol separates in long, beautifully red needles, resembling chromic acid. This compound, boiled with carbonate of soda solution, yields naphthalic acid.

Nitronaphthalic acid, $C_{10}H_4(NO_2)(OH)O_2$.—This substance is prepared by treating a sulphuric acid solution of naphthalic acid with the calculated quantity of nitric acid. On cooling, it separates out in orange-coloured crystals, which, after washing with water, may be crystallised from alcohol and chloroform. Nitronaphthalic acid crystallises from hot chloroform in bright yellow scales; whilst from benzene it separates in tabular crystals, resembling those of sublimed naphthalene. It is soluble in alcohol, ether, and hot water, and with difficulty in chloroform and benzene. Its aqueous solution, on long-continued boiling, yields hydrocyanic acid, phthalic acid, and a resinous mass. Naphthalic acid melts with decomposition at 157°. Several salts of this acid have been prepared; the barium salt Ba $[C_{10}H_4(NO_2)O_3]_2$, crystallises in orange-red scales, slightly soluble in cold water. The lead salt crystallises in two forms; one in short red prisms, which are difficultly soluble in hot water, and have the composition, $Pb[C_{10}H_4(NO_2)O_3]_2$, and the other in golden yellow needles, easily soluble in water and dilute alcohol, having the composition, $Pb[C_{10}H_4(NO_2)O_3]_2 + 4\frac{1}{2}H_2O$. The silver salt, $AgC_{10}H_4(NO_2)O_3$, is of a dark yellow colour, and easily soluble in hot water.

Amidonaphthalic acid, $C_{10}H_4(NH_2)(OH)O_2$.—This acid is prepared by the reduction of the nitro-acid with tin and hydrochloric acid, or its solution in alcoholic ammonia may be reduced by sulphuretted hydrogen. Amidonaphthalic acid crystallises from hot acetic acid or alcohol in closely-grouped dark-brown needles, from dilute solutions in prisms grouped in nodules; it is but slightly soluble in hot water. On exposure to the air the acid darkens on the surface, acquiring a copper-like lustre, and is no longer soluble in alcohol. Heated to 100° the acid blackens, and at a higher temperature melts and sublimes; the greater portion, however, is carbonised. The salts of the alkaline earths and heavy-metals are difficultly soluble or insoluble in water.

Like other amido-compounds, it forms salts with acids such as hydrochloric acid.

Dioxynaphthaquinone, $C_{10}H_4(OH)_2O_2$, is produced when amidonaphthalic acid is heated with dilute acid in sealed tubes at 170—180° for an hour and a half, and separates on cooling in red-brown spangles, having a metallic green reflection. It crystallises from alcohol in reddish-brown needles, and from glacial acetic acid in dark-red scales, having a metallic reflex. It is also soluble in hot water, separating out completely on cooling. The solutions are red; concentrated solutions have a brownish-red colour; dissolved in ammonia and alkalis, it gives dark-blue solutions, the colour resembling that of the methylated anilines. The solution of dioxynaphthaquinone in soda gives a continuous spectrum when illuminated by magnesium light; in the green and indigo, however, there are a few bright bands. Heated gently, this compound sublimes in cinnabar-red needles, a portion carbonising at the same time. The salts of dioxynaphthaquinone are in general dark-coloured, and, save those of the alkalis, but slightly soluble. Alumina gives a violet-lake; iron salts a dark blue. Heated with acetic anhydride, it yields a di-acetyl-compound, $C_{10}H_4\left\{\begin{matrix}O_2\\(OC_2H_3O)_2\end{matrix}\right.$, showing that it contains two phenol-hydroxyl groups. Dioxynaphthaquinone is oxidised by nitric acid, yielding phthalic acid, thus differing from its isomeride naphthazarin; it appears, therefore, that in the latter the replaced hydrogens are in two different halves of the molecule, and in dioxynaphthaquinone in the same half, it is therefore an α-dioxynaphthaquinone, whilst naphthazarin is β-dioxynaphthaquinone. The constitutional formula of α-dioxynaphthaquinone may be represented as



P. P. B.

Fluoranthene. By A. ATTERBERG (*Deut. Chem. Ges. Ber.*, xi, 1224).—Attention is called to the completeness of the series of aromatic hydrocarbons, commencing with diphenyl, $C_{12}H_{10}$, up to pyrene, $C_{16}H_{10}$. The following are known:—

Diphenyl	$C_{12}H_{10}$
Fluorene	$C_{13}H_{10}$
Phenanthrene	$C_{14}H_{10}$
Fluoranthene	$C_{15}H_{10}$
Pyrene	$C_{16}H_{10}$

E. W. P.

A Hydrocarbon from Styrolene Alcohol. By A. BREUER and T. ZINCKE (*Deut. Chem. Ges. Ber.*, xi, 1403—1407).—In a former communication, the authors have shown that when the α- and β-pinacolins derived from styrolene alcohol are treated with concentrated sulphuric acid diluted with an equal volume of water, a hydrocarbon is formed (p. 886). This hydrocarbon, which has the composition, $C_{16}H_{12}$, crystallises from hot alcohol in slender, shining needles, melting at 101—101·5°. It is easily soluble in the ordinary solvents, volatile in steam, and distils without decomposition at 345—346°. Nitric acid, bromine-vapour, and sulphuric acid react on it, and give substitution-products. Chromic anhydride dissolved in glacial acetic acid oxidises this hydrocarbon, forming a quinone.

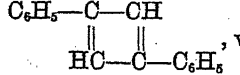
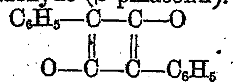
The quinone, which has the composition $C_{16}H_{10}O_2$, crystallises from hot alcohol in beautiful golden-yellow needles, melting at 109—110°, and at higher temperatures volatilises without decomposition. It is easily soluble in the ordinary solvents. It dissolves in the caustic alkalis, forming a green solution, which changes to red on warming; the solution contains the alkali salt of a body melting at 143—144°; probably an oxyquinone. Zinc-dust, in absence of air, decolorises the alkaline solutions. Ammonia in alcoholic solution resolves the quinone into a red substance which melts at 168—170°. The quinone is destroyed when fused with potash or soda. The solutions of this quinone, when exposed to the action of light, undergo a remarkable polymeric change, a body separating out which is best purified by means of chloroform. It melts at 211—211·5°, and, when carefully sublimed, yields the original quinone. Another polymeride is also formed, although in small quantities; it melts about 240°, and likewise yields the original quinone when sublimed.

The authors have not succeeded in obtaining the hydroquinone, but when the quinone is heated to 120—130° with aqueous sulphurous acid, the quinhydrone is formed. This quinhydrone, $C_{32}H_{22}O_4$, forms steel-blue, opaque thick needles; it is soluble in hot benzene, less so in petroleum ether. It is easily oxidised to the quinone, so that when dissolved in alcohol the solution contains nothing but quinone; even the presence of sulphurous acid does not prevent this taking place.

When the quinone is heated with sodium hydrogen sulphite, a body crystallising in colourless needles is formed, which is soluble in alcohol and water, and may be crystallised from the latter if it contains sodium hydrogen sulphite. This compound may be $C_{16}H_8(OH).OSO_3Na$, or $C_{16}H_7(OH)_2.SO_3Na$.

The formula of the hydrocarbon, judging from its boiling point and the constitution of the quinone, is $C_{16}H_{12}$, so that it would be produced by the condensation of 2 molecules of styrolene alcohol, as follows:—

$$2C_8H_{10}O_2 - 4H_2O = C_{16}H_{12}.$$

There are three possible formulæ corresponding with this, of which the following,  $\begin{array}{ccccc} C_6H_5 & - & C & - & CH \\ & & \| & & \| \\ & & HC & - & C & - & C_6H_5 \end{array}$, would explain its formation from phenylacetic aldehyde (β-pinacolin). The quinone would then be formulated thus:  $\begin{array}{ccccccc} C_6H_5 & - & C & - & C & - & O \\ & & \| & & \| & & \\ O & - & C & - & C & - & C_6H_5 \end{array}$. Supposing, however, the hydrocarbon to have the molecular formula, $C_{24}H_{18}$, it must be a triphenylbenzene, and in its formation from phenylacetic aldehyde—3 groups, $CH_2.COH$, unite with the benzene residue C_6H_3, with elimination of 3 molecules of water; and the corresponding quinone would be [illegible], which is not the case. P. P. B.

Isomerides and Derivatives of Camphor and Camphol. By J. DE MONTGOLFIER (*Ann. Chim. Phys.* [5], xiv, 5—118).—In the first part of this paper the author examines the isomerides, in rotatory power, of camphor and borneol, the latter forming, amongst bodies possessed of rotatory power, a distinct series characterised by properties hitherto unobserved. Their isomerism is of two kinds, there being 1. *Camphols of different rotatory power, giving, by oxidation, one and the same camphor;* 2. *Camphols of different rotatory power, giving, by oxidation, isomeric camphors.* The isomeric camphors and the corresponding camphols of the second series range themselves in Pasteur's classification, but the camphols of the first series do not.*

The first part of this paper is divided into two chapters, the first of which is devoted to the isomerides of borneol, and the second to those of camphor.

(1.) ISOMERIC CAMPHOLS.—The rotatory power of camphols from different sources has been very variously given by different authors; thus Berthelot gives $[\alpha]_D = +38°$, Kachler gives $+42°$, and Riban $+2° 36'$; the first having been prepared by the action of alcoholic potash on camphor, and the others by the action of sodium. Riban attributes his result to a loss of rotatory power in the action of sodium, but the author proves that the camphol thus obtained regenerates the original camphor with its rotatory power unchanged. Pasteur has shown that bodies possessed of rotatory power are susceptible of four possible isomeric modifications, viz., dextrorotatory, lævorotatory, racemic formed by their combination, and inactive; but in the present case, none of these can be present except the dextrorotatory. The author therefore attributes these various rotatory powers to the formation of a new inactive modification, formed by the union of ordinary dextrorotatory camphol with an instable lævorotatory camphol possessing an equal and opposite rotatory power, and capable of being converted into dextro-camphol by etherification at high temperatures, and into dextro-camphor by oxidation.

Borneol prepared by the action of alcoholic potash on camphor at a temperature of 180—210° has a rotatory power of $2° 58'$—$1° 41'$; a second treatment with alcoholic potash raises it to $5° 15'$, which the author attributes to the formation of liquid products. When the alcohol employed is weak, the rotatory power becomes as high as $+19° 45'$.

Four experiments on the preparation of borneol by means of sodium, in which the temperature and the energy of the reaction were varied, gave products whose rotatory power varied from $+10° 18'$ to $1° 26'$. The first portions of borneol deposited had a much greater rotatory power than the later portions, which were sometimes strongly lævorotatory.

The author concludes from these experiments, and from the fact that sodium-camphol when heated alone always increases in rotatory power, that the borneol prepared either with sodium or with alcoholic potash would be perfectly inactive if secondary reactions did not take place which give rise to active products.

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* This statement is contradicted in the conclusions at the end of the paper.—*Abstractor's note.*

Instable Lœvo-camphol.—This is easily prepared by fractional precipitation of the products which are deposited during the decomposition of the borneo-carbonate, the dextro-camphol going down first. By employing 100 grams camphor, 300 toluene, and 15 grams sodium, a final product of 3 grams is obtained having a rotatory power of − 23° 54′ to − 21° 44′. By employing larger quantities of material and operating in a slightly different way, 45 grams were obtained having a rotatory power of − 23° 30′ to − 34° 12′. The rotatory power of the absolutely pure product is probably −37°, corresponding with that of the dextro-camphol.

When this lævo-camphol was heated with stearic acid, and the product decomposed by lime and examined, it was found that when the temperature was 100° C., the combined camphol had greatly diminished in rotatory power, the uncombined camphol not changing sensibly. At 200° and above, both the combined and the uncombined had diminished in rotatory power, and when the treatment with stearic acid is repeated, the lævo-camphol is converted in great part into dextro-camphol.

The transformation of the uncombined camphol may be attributed either to the action of water (which is separated in the reaction) or to that of heat alone. To determine this, the actions of these two agents were examined, and it was found that when this lævo-camphol is heated with water at 200° for 19 hours, its rotatory power becomes absolutely *nil*. The action of heat alone is still more powerful, for the lævo-camphol of rotatory power − 21° 44′, becomes dextro-camphol of rotatory power + 33° 54′ when heated at 220° for 24 hours.

It appears, therefore, that when this lævo-camphol is heated, it is converted partially into dextro-camphol, which, in presence of water, unites with the residual lævo-camphol to form the inactive variety; the water acts merely as an absorbent of the heat produced in the reaction, which, in its absence, completes the transformation of the lævo- into dextro-camphol. This instable lævo-camphol, when oxidised by nitric acid, is entirely converted into ordinary dextro-camphor ($[\alpha]_D = + 41° 8'$).

Inactive by Compensation.[*]—This modification may be obtained as above mentioned, by heating instable lævo-camphol with water at 200°; or by treating the camphol obtained by the action of sodium on ordinary camphor, with stearic acid at a low temperature, the dextro-camphol present in the mixture combining with the stearic acid, and the inactive being left uncombined. This inactive camphol may also be separated from dextro-camphol by fractional sublimation of the same product.

The presence of dextro- and lævo-camphol in this body may be proved either by acting on it with sodium and fractionating the products, or by the action of strong acids, which destroy the lævo-, and leave the dextro-camphol. It resists the action of heat much more than the instable lævo-camphol; and it is proved not to be a racemic combination, for the component parts are of very unequal stabilities, and the compound has nearly the same solubility as the original bodies, for in a mixture of this inactive camphol with dextro-camphol, the portions that crystallise out by evaporation have practically the same rotatory power.

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[*] Formed by the combination of stable dextro-camphol with instable lævo-camphol.

When this inactive camphol is heated at 350°, it changes slowly into dextro-camphol; a mixture of inactive with dextro-camphol of rotatory power + 22° 24′, giving, after 10 hours at 350°, a deviation of + 30°. At 215° no change takes place. When it is heated with water at 200°, a very slight increase of rotatory power takes place. A pure specimen of this inactive camphol, after being heated 24 hours at 200° with half its weight of water, had a rotatory power of about + 1°. A mixture of inactive with dextro-camphol having a rotatory power of 13° 15′, gave, after 9 hours' heating at 275°, a deviation of 14° 18′.

When this inactive camphol is heated with stearic acid for 10 hours at 200°, for 25—30 hours at 150°, or for 120—140 hours at 100°, an increase of rotatory power takes place in the portion which combines with the stearic acid, whilst the uncombined portion undergoes little or no change. This increase is the greater the higher the temperature, so that at 275° it amounts to 37°, which is the rotatory power of stable dextro-camphol. The increase of rotatory power is nearly the same at all temperatures below 200°; above that, it is greater the higher the temperature, but is not influenced by the duration of the heating, proving that it is the etherification and not merely the heat which increases the rotatory power.

The increase of rotatory power of this instable inactive camphol at a temperature (t) above 200° may be found by the equation—

$$[\alpha]_D = +59^\circ\ 5' - 0{\cdot}6395\ t + 0{\cdot}00191\ t^2,$$

which may also be applied to any camphol by adding its original rotatory power to the theoretical increase.

When mixtures of this inactive camphol with dextro-camphol having a moderate rotatory power are heated with twice their weight of stearic acid for 20—30 hours, according to the temperature, the dextro-camphol unites with the acid more rapidly, and the uncombined camphol has either a very small rotatory power or in many cases is perfectly inactive. Mixtures of inactive with a very small quantity of dextro-camphol cannot be separated in this way. Occasionally a lævorotatory action is developed, but in this case the camphol may be rendered completely inactive by heating for a short time with water at 200°.

General Action of Acids on Inactive Camphol (by Compensation).—The etherification of this inactive camphol can give three different results as regards rotatory power:—

(1.) Little or no action, by anhydrous acids at low temperatures.

(2.) Transformation into dextro-camphol by anhydrous acids and by weak acids, such as stearic acid.

(3.) Transformation into inactive camphol and camphene by strong acids, and by weak acids at high temperatures.

At the same temperature the action is the more energetic as we use a stronger acid (putting aside anhydrides); for example, at 200° stearic acid transforms this inactive camphol partially into dextro-camphol; benzoic acid transforms it almost entirely into dextro-camphol; and acetic acid gives only the true inactive camphol and camphene. For the same acid, the transformation into dextro-camphol is the more complete as we use a higher temperature; and when once the temperature is reached at which the true inactive camphol is formed, more camphene and less inactive camphol are formed as the temperature becomes higher.

Camphyl Acetate.—This ether is prepared by heating 3 parts camphol with 2 parts acetic anhydride for 8—10 hours at 150° in sealed tubes. Under these conditions the materials unite entirely. The product is purified by washing with water, drying, and distilling, the part coming over at 225—227° being the pure product. Prepared from dextro-camphol (+37°) it is an oily liquid, insoluble in and lighter than water, boiling at 227°, and having a peculiar odour, recalling that of camphol and acetic acid. On standing for a long time it crystallises entirely in needles melting at 24°; its rotatory power is slightly less than that of the original camphol (about + 32°). Its composition is represented by the empirical formula $C_{12}H_{20}O_2$. Caustic potash and metallic sodium decompose it, regenerating the original camphol.

If instead of pure dextro-camphol an artificial camphol of small rotatory power be employed, a product is obtained which refuses to crystallise in a freezing mixture, unless some of the crystals of the pure substance are dropped into it, whereupon needles begin to separate, which can be removed from the remaining liquid. If the temperature is allowed to rise they re-dissolve immediately. The rotatory powers of these ethers vary with the camphol employed; their boiling points are the same as the preceding, and their density 0·990 at 13°. They have not, however, been obtained in an absolutely pure state.

Dextro-camphol is most easily obtained in the pure state by the action of stearic acid on camphol (prepared with alcoholic potash) at 275°. Its rotatory power is $[\alpha]_D = +37°$ (about 42° for the transition tint), the same as that of natural borneol. It varies with the dilution of the liquid, the variation being about the same as that of camphor. Dextro-camphol is very stable; it is modified only by mineral acids. By oxidation, it reproduces dextro-camphor. Strong organic acids etherify it almost without alteration. A temperature of 350° continued for 16 hours alters its rotatory power from +37° to +34° 45′, due to the formation of stable lævo-camphol.

Inactive Camphol.—This camphol cannot easily be obtained pure. The best process is the treatment of pure instable lævo-camphol with crystallisable acetic acid at 200°, but the preparation of the lævo-camphol is extremely troublesome. Another process is to separate it from its admixture with dextro-camphol by means of acetic acid.

Inactive camphol has the same physical properties as the preceding camphols, but is a little softer and less crystalline. With acetic acid it gives a liquid ether, but no camphene. Its formation immediately precedes the breaking up of instable lævo-camphol into water and camphene. It is the most stable of the camphols.

General View of the Isomerides of Camphol.—The discovery of instable lævo-camphol greatly simplifies the question of isomerism, if, as seems probable, it is not an isolated type. Bodies possessing rotatory power can be arranged in two classes, the stable and the instable, and the very fact of the existence of these instable bodies might explain many cases of isomerism. For instance, among the numerous bodies of the formula $C_{10}H_{16}$ there are many presenting no distinct relation to one another in rotatory power, but it is possible that these cases may sometimes be explained by regarding those bodies as mixtures; in many others they may be more or less stable and susceptible of modification.

From experiments not given in this paper, the author considers it probable that there are in the lævo-series bodies corresponding with those which he has described in the dextrô-series, but the rarity of lævo-camphor and the difficulty attending its artificial production have prevented exact experiments on this subject.

There are, therefore, the following nine isomeric camphols:—

1. Stable dextro-	Dextro-rotatory class.
2. Instable lævo-	
3. Their combination	
4. Stable lævo-	Lævo-rotatory class.
5. Instable dextro-	
6. Their combination	
7. Combination of stable dextro- and lævo-	Racemic class.
8. Combination of instable dextro- and lævo-	
9. True inactive.	

The bodies 1, 2, 3, and 9 are those described in the present paper. The madder-camphol of Jeanjean is doubtless stable lævo-camphol mixed with a little dextro-camphol, and the camphol discovered in amber by Berthelot and Buignet seems to be the racemic No. 7, also mixed with a little dextro-camphol.

(2.) Isomeric Camphors.—The camphor which is found in many natural essences differs from ordinary camphor only in its rotatory power, and the same essence often gives camphors with different rotatory powers. Thus Lallemand (*Ann. Chim. Phys.* [3], lxvii, 412) obtained from essence of rosemary a camphor of rotatory power +30°, and the author himself obtained the numbers +21° 24′, + 21°, and + 10° 30′ from camphors from the same essence. He considers that these different rotatory powers are due to mixtures in different proportions of ordinary dextro-camphor and lævo-camphor (from chamomile).

To prove this, the following experiments were made. A camphor of rotatory power +10° 30′ was converted into camphol by means of alcoholic potash, and the camphol purified by stearic acid. In the first experiment the rotatory power of the purified camphol was −2° 39′, in the second −1° 45′; these two camphols when mixed and oxidised by nitric acid gave a dextro-camphor +4° 42′. The camphol not combined with stearic acid was purified by a second treatment and oxidised, and gave a camphor +12° 43′, thus showing that some of the lævo-camphor in the original camphor is separated by the above treatment.

Ordinary camphor of rotatory power 40° to 42° increases also in rotatory power when purified by the above treatment, one of 41° rotatory power having a rotatory power of 43° 37′ after purification.

When sodium is used for the conversion of camphor into camphol, these results are not obtained, dextro-camphor being attacked with the same rapidity as lævo-camphor.

When camphor, pure and dry, is heated in sealed tubes to 350° a constant, though slight, decrease in rotatory power is observed, which the author attributes to the formation of the racemic isomeride of camphol.

The experiments of the author, on the variation in rotatory power of camphor by dilution, using benzene and alcohol of 90 per cent., lead to the following equations for ordinary camphor (*e* being the proportion of solvent relative to one part of solution):—

Benzene .... $[\alpha]_D = 52{\cdot}1° - 12{\cdot}6\,e$.
Alcohol of 90 per cent. $[\alpha]_D = 51° - 11{\cdot}75\,e$.

For pure dextro-camphol, with alcohol of 95 per cent., the equation is $[\alpha]_D = 55° - 12{\cdot}7\,e$; for rosemary camphor $[\alpha]_D = 13{\cdot}1 - 2{\cdot}9\,e$.

From these results it will be seen that a change of solvent makes but little difference to the variation of rotatory power; and on the other hand, that all the curves referring to alcoholic solutions are nearly parallel, from which it may be concluded that all the different camphors have the same variation of rotatory power.

If the preceding variation be compared with that of borneol (solvent, absolute alcohol; dextro-camphol mixed with inactive camphol by compensation), $[\alpha]_D = + 28{\cdot}8° - 7{\cdot}4\,e$, or that of patchouli camphor (Montgolfier, *Compt. rend.*, lxxxiv, 88), $[\alpha]_D = 124{\cdot}5° + 21\,e$, it will be seen that the first is practically the same as that of camphor, and that both are inversely proportional to their equivalents.

The equivalents of camphor, camphol, and of patchouli-camphor being respectively 152, 154, and 222, or 4·1, 4·1, and 6, the variation of rotatory power is $\frac{1}{43}$, $\frac{1}{39}$, $\frac{1}{6}$. The variations of rotatory power may perhaps be attributed to feeble combinations, which are decomposed on changing the proportions of solvent, and, although these three substances are very different in properties, the heat-work necessary to the formation of these combinations may be of the same nature, and be in relation to the equivalent.

It is known that camphor forms compounds with nitric acid, hydrochloric acid, &c.: when camphor is added little by little to hydrochloric acid it seems first to dissolve, but an oily layer soon separates, which is a compound of the two; the dilute alcoholic solution of camphor sometimes separates into two layers. Camphol and patchouli-camphor behave in the same way, the latter on addition of water to its alcoholic solution.

(3.) PRODUCTS OF OXIDATION OF CAMPHOR.—Berthelot, in characterising the class of bodies which he calls *Carbonyls*, makes them differ from ordinary aldehydes and from ketones in that, by direct oxidation, they do not give a monobasic acid comparable with acetic acid; camphor, for instance, treated with nitric acid or permanganate, gives only camphoric acid, $C_{10}H_{16}O + O_3 = C_{10}H_{16}O_4$. The author, however, employing sodium-camphor instead of camphor itself, has obtained, by the simple action of the air, camphic acid, an intermediate acid, and camphoric acid. The intermediate acid (oxy-camphic) is not indeed obtained under the above conditions, but it is formed by the action of potassium permanganate on camphic acid. The following is the series of reactions accomplished:—

$C_{10}H_{16}O + O = C_{10}H_{16}O_2$ (camphic acid).
$C_{10}H_{16}O_2 + O = C_{10}H_{16}O_3$ (oxy-camphic acid).
$C_{10}H_{16}O_3 + O = C_{10}H_{16}O_4$ (camphoric acid).

A few details on the properties of the first two acids will first be given, then the processes for the transformation of sodium-camphor into camphic and camphoric acids, and of camphic into oxycamphic and camphoric acids. Camphoronic acid, a product of the oxidation of camphoric acid, and phoronic acid, a product obtained from camphic acid, will then be described, and the crystalline form and some new properties of anhydrous camphoric acid will be given.

Camphic Acid.—This acid, when prepared by Berthelot's process, contains a certain proportion of another acid, which is left undissolved on treating the camphic acid with carbon bisulphide. After purification in this way, camphic acid is but slightly soluble in cold water, more so in hot water, very soluble in alcohol, ether, &c.; from its solution in hot water it separates in woolly flocks, which collect together after some time. It is a very viscid liquid, which after long standing solidifies to a hard, brittle mass. Its rotatory power is $[\alpha]_D = 15° 45'$. It decomposes on heating to 250°, giving water, oily hydrocarbons, and a viscid acid heavier than water. The liquid products separate into two parts, one boiling at 215° (its analysis leads to the formula $C_{14}H_{24}$, but it is not pure), the other at 260°. When heated for some hours at 200° with ten times its weight of water, it gives a viscid liquid of colophenic odour. Prolonged heating with hydrochloric acid at 100° has a similar effect. It is not converted into campholic acid by hydrogenation. By oxidation with permanganate it yields camphoric and other acids; by oxidation under different conditions, in presence of air and caustic potash, it yields the acid insoluble in carbon bisulphide mentioned above.

The camphates of lead, zinc, silver, and copper, are nearly insoluble in cold water, soluble in alcohol, &c. The copper salt is formed by double decomposition between sodium camphate and cupric sulphate; it is a green powder, unalterable at 140°; above that temperature it melts to a black liquid, which subsequently decomposes. It is partly soluble in strong alcohol, in benzene, ether, and chloroform. The alcoholic solution is green, and on standing separates into two layers, the upper of which is aqueous alcohol, and the lower a strong solution of an acid cupric camphate, $C_{10}H_{16}O_2.2C_{10}H_{15}CuO_2$. The part undissolved by alcohol is doubtless a basic salt.

Oxycamphic acid, $C_{10}H_{16}O_3$, is found among the products of the oxidation of camphic acid, which it greatly resembles, but is more liquid and more soluble in water. It seems also to be produced in the action of nitric acid on camphic acid, and in other reactions.

The metallic oxycamphates are insoluble in water, but soluble in alcohol, &c.

Action of Oxygen on Sodium-camphor.—When sodium-camphor is dissolved in a hydrocarbon (xylene), and subjected to a current of dry air, it blackens, and yields on purification camphic and camphoric acids, and a resin. With a small quantity of air, camphic acid and the resin are almost the sole products; with an excess of air, camphoric acid is produced. The resin is solid, brittle, and fusible below 100°; towards 250° it decomposes with production of colophenic compounds and anhydrous camphoric acid.

By passing a large excess of air through the solution of sodium-camphor, distilling off the hydrocarbon, and precipitating with an acid, a nearly solid product is obtained; this on distillation yields a liquid, which on standing deposits crystals having the composition of camphoric anhydride, $C_{10}H_{14}O_3$, melting at 213—215°. It is slightly soluble in cold, more so in boiling alcohol, from which the compound is deposited on cooling in long needles, insoluble in cold alkalis, slowly soluble on heating, forming solutions of alkaline camphorates.

By treating camphic acid with rather more than its own weight of potassium permanganate, and purifying the product by extraction with ether, sublimation, &c., a quantity of camphoric acid equal to about 4 per cent. of the camphic acid used, may be obtained. Oxycamphic, acetic, and another acid (crystallising from alcohol in concentric groups of needles, and from ether in long needles; perhaps toluic acid) are formed at the same time.

Oxycamphic acid treated with permanganate also yields camphoric acid.

Phoronic Acid.—This acid is contained in crude camphic acid in the proportion of 3—5 per cent., and is separated from camphic acid by treatment with carbon bisulphide, in which the new acid is totally insoluble. After purification with alcohol and animal charcoal, it forms laminæ and thick tables, having the composition expressed by the formula $C_9H_{16}O_2$, being formed from camphic acid by the reaction $C_{10}H_{16}O_2 + O_2 = C_9H_{16}O_2 + CO_2$; it may be regarded as formed from phorone by the addition of water, $C_9H_{14}O + H_2O = C_9H_{16}O_2$, in the same way as campholic acid is formed from camphor.

Phoronic acid melts at 168—169°, and solidifies at a slightly lower temperature; at a higher temperature it boils, and distils without alteration. It is nearly insoluble, even in boiling water, very soluble in alcohol, insoluble in carbon bisulphide; with bromine it gives viscid products; nitric acid attacks its violently. Its salts are soluble in alcohol, mostly insoluble in water. Its rotatory power is $[\alpha]_D = +23°$.

Its formation from camphic acid is proved by the following experiments:—Perfectly pure camphic acid was dissolved in alcoholic potash, and heated in a sealed tube at 180° for 10 hours; the camphic acid reprecipitated and treated with carbon bisulphide left an insoluble powder, presenting the crystalline form and melting point of phoronic acid, but in quantity too small for analysis.

A strongly alkaline aqueous solution of camphic acid, heated in a sealed tube at 100° for 9—48 hours, absorbs a considerable quantity of oxygen, without the formation of camphoric acid; the author therefore considers that the formation of phoronic acid cannot be doubted.

Camphoronic acid is found in the mother-liquors of camphoric acid, from which it may be extracted by Kachler's method. Its rotatory power is $[\alpha]_D = -18° 42'$, and seems to diminish slightly by dilution. This acid and phoronic acid are the only examples of rotatory power remaining in an oxidation derivative containing less carbon than the original body.

The mother-liquors contain also a considerable quantity of camphoric acid, which may be extracted by adding an acid and ether. After purification, this acid has a rotatory power $[\alpha]_D = 48° 12'$. The rotatory power of camphoric anhydride is $[\alpha]_D = -7° 7'$. The crystals of camphoric anhydride belong to the orthorhombic system; the angle of the prism is 120° 25′.

ACTION OF ZINC CHLORIDE ON CAMPHOR.—The products examined were those boiling at temperatures above the boiling-point of cymene, and those which boil below that of toluene, the special object of the examination being to determine whether laurene is formed in this reaction.

The portion boiling above cymene contains two hydrocarbons, one boiling at 335°, the other at 195°. The one boiling at 335° is an oily liquid, insoluble in and lighter than water, of faint, minty odour, solidifying at a few degrees below 0°. Its analysis leads to the formula, $C_{20}H_{28}$; it is probably a dicymene.

The hydrocarbon boiling at 195° is Fittig's laurene; according to the author it is an isomeride of cymene, having the formula $C_{10}H_{14}$. It forms a conjugated sulpho-derivative, the barium salt of which has the composition $C_{10}H_{13}BaSO_3 + 2H_2O$, ordinary barium sulphocymenate being $C_{10}H_{13}BaSO_3 + 1\frac{1}{2}H_2O$. The two salts differ also in their solubilities, that of ordinary barium sulphocymenate being 1 part in 44·94 of water at 16°, and that of the new salt being 1 part in 39·86 of water at 16°.

On adding bromine to this hydrocarbon, a brisk action takes place, and white crystals separate, which, after recrystallisation from boiling alcohol, melt at 201° and solidify at 200°. Their composition is represented by the formula $C_{20}H_{12}Br_2$; treated with bromine they give a tribromide, which was not obtained quite pure. Fittig obtained from his laurene a tribrominated derivative, $C_{11}H_{13}Br_3$, melting at 125°, but the author considers that it must be the present compound, $C_{10}H_{11}Br_3$; he also never found among the hydrocarbons boiling between 177° and 200° any but those of the formula $C_{10}H_{14}$. On treating these with bromine, needles of $C_{10}H_{12}Br_2$ are formed, accompanied by a liquid dibromo-derivative which does not form crystals on further addition of bromine, as Fittig's laurene would do.

Jannasch, by treating with sodium a mixture of methyl iodide and monobromo-mesitylene, obtained a liquid tetramethylbenzene, boiling at 192°, which when treated with bromine gave a dibromo-derivative, $C_{10}H_{12}Br_2$, melting at 199°, very slightly soluble in cold alcohol, more so in hot alcohol, crystallising in brilliant needles, agreeing thus in all the characters of both the hydrocarbon and its dibromo-derivatives with the compound which has been described by the author. The action of zinc chloride on camphor thus produces tetramethylbenzene, $C_6H_2(CH_3)_4$, together with cymene, which appears to be a methyl-propyl-benzene.*

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* This view of the constitution of cymene was established by Fittica five years ago (*Liebig's Annalen*, 1873, lxxii, 303).—ED.

Rommier found in coal-tar two cymenes boiling respectively at 175° and 195°, which seem to be formed in a manner analogous to the present.

Among the products of the action of zinc chloride on camphor, which boil at temperatures below the boiling-point of toluene, are benzene (recognised by Berthelot's method), hexylene, and an oxygenated compound.

The main gaseous product of this action is marsh-gas, formed probably according to the equation $C_{10}H_{16}O = C_7H_8O + 2CH_4 + C$, its formation thus being simultaneous with that of a phenol. Ethylene and its homologues are not formed.

Zinc chloride therefore acts in three ways on camphor:—1. Regularly, giving cymene, dicymene, and tetramethylbenzene. 2. By destroying the carbon-group, giving lower homologues of cymene. 3. By breaking up the carbon group in a different way to the preceding, giving phenols and homologues of acetylene.

(4.) ACTION OF ALKALIS ON CAMPHOR.—The action of alkalis on camphor varies according to the conditions of the experiment: with alcoholic potash, camphol, and camphic acid, or a complex liquid are formed; with potash alone at a high temperature, campholic acid is produced.

Campholic acid, $C_{10}H_{18}O_2$, is formed on heating sodium-camphor in sealed tubes at 280°, and after purification forms crystals, melting at 105—106°, solidifying at 103°, and boiling at 253—255° (uncorrected); rotatory power, $[\alpha]_D = + 49° 8'$. It is formed by the action of camphor on sodium-camphol, according to the equation $C_{10}H_6O + C_{10}H_{17}NaO = C_{10}H_7NaO_2 + C_{10}H_{16}$ (or a polymeride), a reaction depending on the instability of sodium-camphol, to which also the author refers the method of preparation of campholic acid devised by Malin (*Ann. Chem. Pharm.*, cxliv, 201), and afterwards studied by Kachler (*Deut. Chem. Ges. Ber.*, v, 175). A specimen of campholic acid prepared according to Delalande's method melted at 98° and had a rotatory power of + 45° 32'; Delalande gave 88° as the melting point. Campholic acid crystallises in fragile prisms belonging to the monoclinic system, generally lengthened normally in the plane of symmetry, striated longitudinally; a series of angular measurements is also given.

The liquid before mentioned as formed in the action of alcoholic potash on camphor, boils after purification at 238—240° (corrected), and does not solidify in a powerful freezing mixture. Analysis leads to the formula $C_{15}H_{24}O$, which is that of a body formed by the action of camphor on camphol in presence of alcoholic potash, according to the equation $2C_{10}H_{16}O + C_{10}H_{18}O = 2C_{15}H_{24}O + H_2O$, which is equivalent to $2C_{10}H_{16}O + C_{10}H_{16} = 2C_{15}H_{24}O$, or more simply, $C_{10}H_{16}O + C_5H_8 = C_{15}H_{24}O$; a reaction which shows the passage of bodies containing C_{10} into bodies containing C_{15} by the introduction of the group C_5H_8; moreover it is a step in the synthesis of some natural bodies; for by adding H_2 to this new body, we have $C_{15}H_{26}O$, an isomeride of cedar-oil and the camphors of cubebs and patchouli.

If dilute alcoholic potash be used in this reaction, the liquid formed boils at 160°, and is either terebene or an isomeride thereof.

NEW METHOD OF CONVERSION OF CAMPHOR INTO CAMPHENE.—When the compound obtained by the action of phosphorus pentachloride on camphor is treated with sodium, a camphene is formed, according to the equation $C_{10}H_{16}Cl_2 + Na_2 = C_{10}H_{16} + 2NaCl$. The melting point of this camphene is 57—59°, instead of 45—47°, that of ordinary camphene. It combines with hydrochloric acid to form a crystallised hydrochloride, $C_{10}H_{17}Cl$, melting at 147° (taken in hydrochloric acid gas), and rapidly losing hydrochloric acid on exposure to the air; heated with alcoholic potash, or even with water, it regenerates camphene.

The rotatory power of this camphene is $[\alpha]_D = + 44° 13'$, differing therefore in this respect from camphene prepared in other ways, which is always inactive to polarised light.

It will have been observed that the body $C_{10}H_{16}Cl_2$ is considered to be formed in the action of PCl_5 on camphor, contrary to Pfaundler's assertion, and according to Gerhardt's equation, $C_{10}H_{16}O + PCl_5 = POCl_3 + C_{10}H_{16}Cl_2$; in fact, if it were the body $C_{10}H_{15}Cl$, that is formed in this reaction, the action of sodium on it would not give exclusively camphene, as is the case with $C_{10}H_{16}Cl_2$.

The compound $C_{10}H_{15}Cl$ is easily prepared by the action of water on $C_{10}H_{16}Cl_2$. It has a rotatory power, $[\alpha]_D = -4°$; with sodium it gives camphene mixed with cymene, $2C_{10}H_{15}Cl + Na_2 = C_{10}H_{14} + C_{10}H_{16} + 2NaCl$.

It appears from the above facts that Louguinine and Lippmann's process for the preparation of pure cymene must always give cymene mixed with camphene, since sodium is used to destroy the last traces of chlorine-compound; in fact, the author has discovered camphene in cymene prepared by this method.

CHLORO- AND BROMO-DERIVATIVES OF CAMPHOR.—*Monobromocamphor.* —This compound is but slightly soluble in cold alcohol, and is precipitated from this solution by water in slender needles. It is very soluble in chloroform, carbon tetrachloride, benzene, &c.; it dissolves in sulphuric acid and is reprecipitated unchanged by water; nitric acid does not attack it in the cold or even on boiling for a few minutes. Its rotatory power is $[\alpha]_D = + 139°$. Treated with a 2 per cent. sodium-amalgam it regenerates camphor. Heated a few degrees above its melting point it sublimes in very thin needles. Its crystalline form is a monoclinic prism, lengthened normally in the plane of symmetry. The plane of the optic axes is perpendicular to the plane of symmetry. The dispersion is not apparent.

In the preparation of monobromocamphor, a viscid liquid is often obtained which solidifies after long keeping to a crystalline mass. It consists principally of monobromocamphor mixed with other bodies very soluble in alcohol. One of these is an isomeride of monobromocamphor, similar to Wheeler's monochlorocamphor, *i.e.*, losing hydrobromic acid under the influence of the weakest agents, and furnishing oxidation products. There is also probably oxycamphor in this mixture, formed from the above body by the action of the moisture of the air.

Dibromocamphor is best prepared by heating 1 part of camphor with 4 parts of bromine in sealed tubes at 100°. The liquid produced slowly gives off hydrobromic acid on exposure to the air and deposits dibromocamphor. The properties of this body are nearly the same as those of the monobromo-compound. The rotatory power is +102°. The rotatory powers of these two bromine-compounds are thus inversely as their equivalents, a relation which does not exist in the other camphor-derivative. By slow crystallisation from alcohol or chloroform, dibromocamphor is obtained in fine tabular crystals, which are rectangular prisms with rhombic bases of 128° 24′; there are no hemihedral faces.

Chlorine Derivatives of Camphor.—Wheeler, by the action of hypochlorous acid on camphor, obtained a monochlorocamphor, but the action does not stop there, a dichlorocamphor, and even higher compounds, being formed; gaseous chlorine acts in a similar way.

CONCLUSIONS.—In the first part of this research the question of the isomerides of camphor is definitely settled by the discovery of instable lævo-camphol, the results in reference to which may be summed up as follows:—

1. The hydrogenation of camphor gives rise, under all conditions, to two distinct camphols.

2. These two camphols are formed in equal proportions, have equal and opposite rotatory powers, and reproduce by oxidation the same camphor. They differ in their stability, the first being only changed with difficulty, the second giving rise, according to the energy of the reaction, to a camphol inactive by compensation, to the active stable camphol of opposite rotatory power, to real inactive camphol, or finally, to camphene.

3. These transformations are produced either by the action of heat, or by the entry of the instable camphol into chemical combination. Etherification gives the best results, and, under otherwise similar circumstances, the change is greater as the temperature is higher and the acid employed more energetic.

4. It is thus evident that to stable dextrocamphol corresponds an instable lævo-, and *vice versâ;* and these isomerides being capable of forming compounds analogous (to a certain extent) to racemic modifications, there are nine isomerides of camphol, all of which, however, can enter into the four types distinguished by Pasteur.

5. The types inactive by compensation (not the racemic) are allied to the active type by their transformations, as well as to the racemic type by their composition, mode of transformation, and stability, which is much greater than that of pure instable camphols.

As to the isomerides of camphor, it appears that the same essence may furnish camphors of different rotatory power, this difference being due to mixtures in variable proportions of dextro- and lævo-camphor.

Finally, it may be concluded, from these researches, that stability of rotatory power depends directly on chemical stability. In the second part of this memoir a new method of formation of the acids derived from camphor, the true relations of these acids, and a new acid (phoronic) are described. A new isomeride and a polymeride of cymene, formed by the action of zinc chloride on camphor, are also described, their products being in harmony with what is already known of the action of this agent.

It appears from the study of the new active camphene that the camphor obtained by the oxidation of camphene (derived from terebenthene) is isomeric and not identical with Japanese camphor. This isomerism is apparent from the comparison of the rotatory powers of the camphene and camphoric acid, if not of the camphor itself.

C. W. W.

The Quinine Alkaloïds and Potassium Thiocyanate. By F. SCHRAGE (*Arch. Pharm.* [3], xiii, 25—37).—On the addition of potassium thiocyanate to solutions of quinine or cinchonidine salts, a white precipitate is produced which is soluble in excess of either, whereas the precipitate formed in the case of quinidine and cinchonine is not soluble. If the precipitates are produced under circumstances described in the paper, they will be found to be crystalline; the crystals thus obtained are figured and described. Time and degree of dilution appear to influence the crystallisation, whereas temperature does not. The appearance of the crystals when a mixture is under observation is also described.

E. W. P.

Theobromine. By DRAGENDORFF (*Arch. Pharm.* [3], xiii, 1—7).—The husks of the cacao seed yield theobromine, if treated as follows: the extract obtained by boiling them with water is treated with basic lead acetate, and after separation of the precipitate the excess of lead is thrown down by sulphuric acid: the solution is then neutralised with magnesium carbonate, concentrated, and, after the addition of more magnesia, evaporated to dryness. The resulting mass yields theobromine when extracted by alcohol. It has often been found that the murexide test for theobromine is not always successful; but if the precautions be taken—1, that the chlorine-water solution of theobromine is evaporated as rapidly as possible at a temperature not lower than 100°; 2, that the amount of chlorine-water do not vary to a very large amount; the reaction succeeds in all cases.

The solubility of theobromine in water at 100° is .... 1 : 148·5
" " " 17° is .... 1 : 1600
" " in boiling alcohol is .... 1 : 422·5
" " absolute " at 17°.. 1 : 4284
" " in boiling chloroform .... 1 : 105

E. W. P.

Diastase. By M. BASWITZ (*Deut. Chem. Ges. Ber.*, xi, 1443—1445).—By treating an excess of starch with a known quantity of malt-extract and determining the amount of sugar formed, the author thought to be able to draw conclusions as to the amount of diastase present in the malt. When these experiments are made in vessels freely exposed to the air, however, the results vary considerably, owing to the presence of carbonic acid. Experiments were therefore made in a current of carbonic acid and also in an atmosphere free from carbonic acid, from which it appears that the amount of sugar formed is greater in the former than in the latter. The maximum point is reached in about 2½—4 hours. Supposing the formation of sugar from starch to take place as follows: $3C_6H_{10}O_5 + H_2O = C_6H_{10}O_5 + C_{12}H_{22}O_{11}$, then 100 parts of starch should yield 70·37 parts of maltose. If, however, the reaction takes place thus: $4C_6H_{10}O_5 + 2H_2O = C_{18}H_{34}O_{17} + C_6H_{10}O_5$, then 100 parts of starch should yield 80·9 parts of maltose.

The maximum obtained by the author is 67·3, unaltered starch being still present. It would thus appear that the diastase in this reaction uses up a portion of itself, and cannot convert an infinite quantity of starch into sugar. The author concludes that one part of malt is about equivalent to 60—70 parts of dry starch-material. Pressure in presence of carbonic acid influences unfavourably the formation of sugar. P. P. B.

On Gummy Degeneration of Almonds. By G. VULPIUS (*Arch. Pharm.* [3], xiii, 38).—On certain sweet almonds which had been washed and dried, a separation of bassorin was remarked, so that one half of the almond consisted of this substance, whereas the other half was of a hard cartilaginous consistency, and had a brilliant resinous surface. Although gum is often formed in the amygdalin, the above phenomenon does not appear to have been observed hitherto. E. W. P.

The Ferruginous Colouring Matter of Red Wines. By A. GAUTIER (*Compt. rend.*, lxxxvii, 64).—The author re-affirms that the blue colouring matter (*Compt. rend.*, lxxxv, 1507) which he obtained by incompletely saturating wine and then adding sodium chloride, contains nearly 4 per cent. of iron. R. R.

Analysis of the Bulbs of Erythronium Dens Canis (L.). By DRAGENDORFF (*Arch. Pharm.* [3], xiii, 7—13).—The analysis of the bulbs of the above plant, which is used for food and medicine in Siberia, is as follows:—

Moisture	9·405	per cent.
Ash (containing 24 per cent. P_2O_5)	1·169	,,
Cellulose	2·575	,,
Vasculose, cuticulose, &c.	0·859	,,
Starch	51·247	,,
Glucose (soluble in alcohol)	4·801	,,
Glucose (soluble in water after removal of the above glucose by alcohol)	9·516	,,
Carbohydrate (arabic acid ?), easily transformed into glucose soluble in water	9·085	,,
A dextrin-like substance	3·390	,,
Metarabic acid	0·954	,,
Citric and tartaric acids	0·520	,,
Oxalic acid	trace	
Albumin	0·011 ?	,,
Albuminous matter insoluble in water	5·162	,,
Fat	0·135	,,
Resin	1·045	,,
	99·874	,,

Neither saponin nor alkaloïds were found. E. W. P.

Physiological Chemistry.

Digestion of Cellulose by Geese. By H. WEISKE and T. MEHLIS (*Landw. Versuchs-Stat.*, xxi, 411—423).—From experiments in which two geese were fed with *Leontodon taraxacum* and *Equisetum arvense*, it appears that the cellulose of these plants is not digested by geese. J. T.

Constitution of Malt Liquors and their Influence upon Digestion and Nutrition. By J. J. COLEMAN (*Chem. News.*, xxxvii, 177—181).—When starch and starch-foods, as bread, potatoes, &c., are digested for some hours with malt liquors which have been made faintly alkaline, there is a certain amount of starch given up to solution; and in the author's experiments with bread and various kinds of malt liquors, the amount dissolved varied between 15 and 60 per cent. of the starch present. To this digestive action of malt liquors, or their power to influence the digestion of other food, the author ascribes their fat-producing property, and not to the extractive matter, which is too small in quantity to be of great food-value.

The solvent action of malt liquors in this manner is probably due to some ferment such as diastase, which has escaped destruction in the brewing operation. This supposition is supported by the results of the experiments, which showed that it was not the richest ales which had the most digestive action, but those malt liquors, such as porter, &c., which were poor in alcohol, and probably contained more diastase.

A. J. C.

Formation of Glycogen in the Liver. By J. MAYER (*Pflüger's Archiv. f. Phys.*, xvii, 164—182).—Experiments were carried out upon rabbits which had fasted for four or five days. Grape-sugar was injected into a vein, and after a certain number of hours blood was taken from the carotid artery or jugular vein. Urine was also removed by pressure. The amount of sugar in the blood and urine was determined, the animal was killed, and the amount of glycogen in the liver was estimated. The author finds that it is not necessary that blood highly charged with sugar should be sent directly by the mesenteric vein into the liver, in order that glycogen should be produced therein, but that the presence of a small quantity of sugar in the general system is sufficient.

Ludwig and Scheremetjewsky have shown that sugar brought into the circulation is not oxidised by the oxygen of the alkaline blood. The author's researches have now proved that sugar is stored up as such, or in the form of glycogen, in parts of the organism other than the liver and blood.

In agreement with v. Mehring's results, the author found that the blood of rabbits whose livers contained no glycogen may yet contain sugar. This observation holds only in the case of rabbits which have fasted not more than seven days; after eight to ten days' fasting, no sugar could be detected in the blood. Experiment showed that no appreciable decomposition of sugar present in blood had taken place after 20 to 30 minutes from the time of removal from the artery.

Experiments were also carried out upon rabbits in which the spinal cord was severed at different points before injection of sugar into the veins. The general results were as follows :—

Severance of the spinal cord between the fifth and sixth cervical vertebræ, between the last cervical and the first dorsal vertebræ, or between the second and third dorsal vertebræ, does not prevent the partial retention of the sugar in the circulatory system of the animal, where it is employed in the general nourishment of the organism.

Severance of the spinal cord between the fifth and sixth cervical vertebræ exerts a considerable deterrent action upon the formation of glycogen in the liver, but does not cause an increase in the amount of sugar secreted in the urine.

Severance of the cord between the last cervical and the first dorsal vertebra brings about an increased formation of glycogen, but without causing a diminution in the sugar present in the blood withdrawn from the artery.

Severance of the cord between the second and third dorsal vertebræ causes a diminished formation of glycogen in the liver, and at the same time brings about a considerable decomposition, within the organism of the animal, of the sugar injected into the veins.

The estimations of glycogen were carried out by Brücke's method. The liver was broken up in boiling water, and after being ground up for eight or ten minutes with sand, the liquid was boiled, filtered through linen, and the residue washed with boiling water so long as a trace of opalescence was visible. The filtrate was then concentrated, precipitated by addition of mercurio-potassium iodide and hydrochloric acid, filtered, and the liquid decomposed by addition of three volumes of alcohol. After some time the glycogen was collected, washed, first with ordinary, then with absolute alcohol, and finally with ether, and dried at 110° to 115°.

The author finds that the blood from the carotid vein of rabbits normally contains from 0·08 to 0·13 per cent. of sugar.

M. M. P. M.

Toxicological Experiments. By Poleck and Biefel (*Chem. Centr.*, 1878, 334—335).—These experiments were undertaken to determine the amount of the products of combustion of coal, of illuminating gas, and of carbonic anhydride, respectively, which must be present in atmospheric air to produce death. A chamber of 6 cubic metres' contents, and a glass box of 150 litres' capacity were used. The animals experimented on were rabbits, which were put into a small wire-net cage, in which they could move about freely, and so arranged as to admit of the urine being collected. The cage was placed in the middle of the chamber, and a series of glass tubes were so arranged that their openings were in the layer of air breathed by the animal, while their other ends passed through the door of the chamber and were connected with an aspirator in such a manner that the air could be collected in vacuous glass tubes at all stages of the poisoning. The samples so collected were analysed by Bunsen's method. A glass plate was let into the door, so that observations on the animal during the whole course of the experiment might be made. The gases experimented with were allowed to enter the apparatus slowly at some distance from the animals, and were mixed with the air in the chamber by means of a stirring apparatus. When the products of combustion of coal were tried, a small wind furnace, filled with coal or charcoal, and placed in a corner of the chamber, was used.

1. In four experiments in which coal was used, the air after the death of the animal contained on an average 6·56 per cent. CO_2; 0·46, CO; 13·4 O; and 79·58 N. CO spectrum was observed in the blood of all the animals, even of those which had not died. Sugar was found in the urine only in those cases where the poisoning had been very slow. In all cases where the animal had died in from one-half to one and a half hours, no trace of it was discovered.

2. *Coal-Gas.*—In all cases the mixture was explosive. In one experiment death ensued in two hours. The mixture contained 0·08 per cent. CO_2, 0·35, C_nH_{2n}; 2·36, CH_4; 4·42, H; 1·48, CO; 19·15, O; 72·16, N. The gas used contained 2·12, CO_2; 4·85, C_nH_{2n}; 30·8, CH_4; 53·13, H; 6·75, CO; 0·42, O; 1·93, N. H_2S and SO_2 were not found in either case.

Pure carbon monoxide caused death in four different experiments when 1·94, 1·53, 1·65, and 1·02 per cent. were contained in the air. With carbonic anhydride, the air contained 50·41 per cent. CO_2; 10·01, O; and 39·58, N, whilst 0·06, 0·05, and 0·37 per cent. H_2S killed the animals rapidly, and similar results were obtained with carbon bisulphide.

The authors consider that the poisonous property of pure coal-gas is due to carbon monoxide, as hydrogen sulphide is never present, whilst, in the case of coal-combustion, carbonic anhydride, carbon monoxide, and the diminished supply of oxygen work together.

The authors state that they are now engaged in investigating the toxic properties of the gases produced in the manufacture of chlorine, sulphuric acid, &c., &c. J. M. T.

A Poisonous Australian Lake. By G. Francis (*Pharm. J. Trans.* [3], viii, 1047).—On the surface of Lake Alexandrina floats a conferva, *Nodularia spumigera*, allied to protococcus, forming a scum like green oil-paint, some two to six inches thick. This is swallowed by cattle when drinking, causing stupor and unconsciousness, death rapidly ensuing. From the decomposing scum there exudes a blue pigment, which is remarkably fluorescent, being red by reflected, and blue by transmitted light. The spectrum gives a broad and deep band in the red, but shading off to green, quite cutting off orange and yellow. Chemically this colouring matter appears to be allied to that of some lichens. E. W. P.

Experiments on Anaerobiosis with Putrefaction-bacteria. By J. N. Gunning (*J. pr. Chem.* [2], xvii, 266—281).—In a previous paper, the author gave his reasons for doubting Pasteur's assertion that micro-organisms can exist in the absence of free oxygen. The present paper describes his experiments in detail. All the apparatus was made of glass, the different parts being also joined together by glass connections. Large quantities of putrefying bodies—raw flesh, urine, blood, &c.—after being mixed with putrefaction-bacteria, were enclosed in different vessels, oxygen being as far as possible excluded. The vessels were left for at least a week in a room where the temperature was kept steadily at 40°; for the rest of the time—the experiments extended over eighteen months—the temperature varied from 10° to 25°. In some experiments the vessels were exhausted, in others filled with hydrogen or nitrogen; in others, again, bodies were used to absorb the oxygen.

The conclusion drawn from the experiments is that exclusion of oxygen produces the death of the bacteria, and stops the putrefaction; nor does this begin again on admission of air, provided that the latter does not introduce fresh bacteria. G. T. A.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Atmospheric Electricity on the Nutrition of Plants. By L. GRANDEAU (*Compt. rend.*, lxxxvii, 60—63).—Two plants of the same species, and as much alike as possible, were placed under identical conditions, except that one grew in the open air and the other was covered with a wire cage, which permitted the free access of light, air, and moisture, while it completely withdrew the plant from the action of the electricity of the atmosphere; tobacco, giant maize, and Chiddam wheat being the plants operated on. A striking difference was observed in the growth of various kinds of plants thus treated. Those plants withdrawn from the action of atmospheric electricity were much smaller and lighter, and had in the same time elaborated 50 or 60 per cent. less living substance than those grown under ordinary conditions. The former yielded a less percentage of water, and a greater percentage of ash than the latter; but the amount of proteïd matters did not appear to be influenced by the electrical conditions. Plants raised but little above the surface of the ground were as much affected as others by the action of atmospheric electricity. R. R.

The Relation between Nitrogen and Phosphoric Acid in Russian Wheat and Rye. By S. BUBNOFF (*Landw. Versuchs-Stat.*, xxi, 407—409).—Mayer (*Annalen*, ci, 129) found a nearly constant proportion of 1 part phosphoric acid to 2·04 parts nitrogen in wheat grown in Bavaria, whilst for rye the relation was 1 : 2·2. The author found the relation 1 : 2·073 as a mean from five specimens of Russian wheat, and 1 : 2·185 from three specimens of rye. The results obtained also show that the relation is tolerably constant, as Mayer had found previously.

The following numbers show a marked increase in the amount of nitrogen found in wheat, according as the wheat is grown in districts going from west to east:—

Albanian	wheat,	Bavaria............		1·93	per cent.	(Mayer).
”	”	Province of Iver		2·151	”	(Bubnoff).
”	”	”	Charkow	3·98	”	(Laskowsky).
Cuban	”	”	Saratov..	3·98	”	(Bubnoff).
”	”	”	Orenburg	4·25	”	(Laskowsky).

J. T.

Rubidium as a Substitute for Potassium in the Plant-cell. By O. Loew (*Landw. Versuchs-Stat.*, xxi, 389—395).—Nobbe has shown that a substitution of sodium chloride for potassium chloride in the food of plants merely produces the same effect as a want of the potassium salt, whilst lithium chloride kills the plant. Lithium as well as sodium has a lower atomic weight than potassium, whilst rubidium has a higher one, hence it was thought desirable to ascertain the physiological effect of the latter. The experiments made lead to the following conclusions:—

1. Rubidium, either as nitrate or as chloride, cannot satisfactorily replace potassium in the corresponding salt in a food mixture.

2. By the application of rubidium chloride, the plant grows normally up to blooming, then, in consequence of change in the chlorophyll, accumulation of sugar, and defect in the conversion of the latter into starch and cellulose, death gradually ensues, whilst rubidium nitrate, by causing an accumulation of starch, thickens and twists the stem, shortens the plant, curls up the leaves and makes them fleshy, and the plant dies before the flowers appear. J. T.

Formation of Sulphates by the Decomposition of Albumen in Germinating Plants. By E. Schulze (*Deut. Chem. Ges. Ber.*, xi, 1234).—The sulphur originally combined as albumin in young plants grown in the dark is found to be oxidised to a sulphate, the amount depending on the duration of darkness. For instance, after seven days of darkness, half the albuminoïd sulphur is found as sulphuric acid, whereas after only four days the amount of sulphates present is little more than the normal quantity; the rapidity, however, of the change decreases as the growth proceeds. E. W. P.

Composition and Digestibility of Lucerne Hay. By E. Wolff, W. Funke, and O. Kellner (*Landw. Versuchs-Stat.*, xxi, 425—435).—Weiske and Wildt determined the loss in food constituents and the change with respect to digestibility of a lucerne which lay in the field six days, during which it was exposed to two thunderstorms and to one gentle shower of rain. Its composition and digestibility as compared with a carefully dried sample of the same crop, are given below. The loss in dry constituents due to field-drying amounted to 16·7 per cent.:—

	Composition per cent. dry constituents.		Digested by sheep per cent. of the single constituents.	
	Carefully dried.	Field dried.	Carefully dried.	Field dried.
Protein	20·62	18·44	77·84	73·42
Ether extract	3·65	2·32	49·58	32·00
Cellulose	30·34	34·00	34·21	36·57
N-free extract	37·57	37·99	65·26	64·94
Ash	7·82	7·25	—	—

To obtain further data, the authors experimented in 1876 with the following results. 250 kilos. lucerne were carefully dried on a capacious floor. The same quantity was dried in the field. A slight shower fell in the evening of the day on which the plant was cut, and next day a thunderstorm came. After four days the composition was as follows:—

	Air dried.	Dry.
Carefully dried	79·00 kilos.	69·38 kilos.
Field dried	76·25 ,,	64·43 ,,

The latter, therefore, shows a loss of 7·13 per cent. of the dry constituents of the plant. The samples contained:—

	Carefully dried lucerne.	Field dried lucerne.
Protein	17·00	14·94
Cellulose	31·81	33·90
Ether extract N-free extract	43·80	44·22
Ash (free from C and CO_2)	7·39	6·94

The ash contained—

Potash	20·76	18·98
Soda	0·78	0·56
Lime	35·17	31·62
Magnesia	3·11	3·51
Iron oxide	0·81	0·96
Phosphoric acid	9·90	8·39
Sulphuric ,,	6·40	5·37
Chlorine	2·45	2·66
Silica and sand	20·62	27·95
	100·00	100·00

The fodder thus prepared was supplied to sheep, when the following results were obtained for the amount of the different constituents digested, calculated on the 250 kilos. fresh lucerne:—

	Carefully dried lucerne.	Field dried lucerne.
Dry substance	40·71 kilos.	35·04 kilos.
Organic substances	39·12 „	33·98 „
Protein	8·42 „	6·41 „
Cellulose	10·62 „	9·88 „
N-free extract Ether extract	20·19 „	17·63 „
Ash	1·49 „	1·02 „

This gives a loss per cent. of the individual digestible constituents due to field-drying as follows:—

Dry substance	13·93
Organic substance	10·58
Protein	23·78
Cellulose	6·97
N-free extract Ether extract	12·63
Ash	31·54

J. T.

Chemical Composition of Yeast. By Nägeli (*J. pr. Chem.* [2], xvii, 403—428).—Two new methods have been introduced by the author in this investigation. The first consists in treating the yeast with water containing 1 per cent. of phosphoric acid during a very long interval of time: the second method consists in boiling the yeast for considerable periods with successive quantities of water. The exceedingly dilute phosphoric acid solution contained a carbohydrate which the author calls mucus of the fungus germs (Sprosspiltzschleim). This substance is regarded by the author as being produced by the continued action of the acid water upon the cell membranes. Other hypotheses as to the origin of this mucus are discussed by the author. This substance separates in small microscopic globules of very unequal sizes. These globules contain much water; they are coloured brownish-red by iodine; the cell membranes are not affected by the same reagent.

The experiments detailed in the present paper lead to the necessity of distinguishing between the cellulose of the yeast germ and the cellulose of the divided yeast cells, as also between the mucus of the germs and of the cells. The latter, although more plentifully formed during the so-called mucus fermentation, is really not at all a product of fermentation. The mucus of the lactic fermentation is but the membranes of the divided cells. A complete investigation of the liquid obtained by digesting yeast with water containing one per cent. of phosphoric acid during 13 months, showed that it contained α, β, and γ *peptone*, *leucine*, *guanine*, *xanthine*, *sarcine*, *succinic acid*, and small quantities of *albumin*, *carbonic acid*, *alcohol*, and *grape sugar*.

The aqueous extract obtained by repeatedly treating yeast with boiling water was found to contain principally peptones, along with mineral matter and a gum-like substance resembling the so-called dextrin, but differing from this body in optical behaviour, the rotatory power of dextrin being + 223°, whilst the number for the new substance is only + 78°. The gummy body from yeast is easily soluble in hot water, forming a slightly opalescent liquid: it diffuses slowly through parchment, does not reduce Fehling's solution, and is slowly converted into a glucose by the action of acids: it is not precipitated by tannic acid, by borax, nor by lead acetate, unless potash be added. Iodine acts slowly upon this substance, producing a brownish coloration. Nitric acid acts upon the new body with production of a syrupy acid, which is eventually transformed into oxalic acid. No mucic acid is produced in this reaction. Analyses indicate the formula, $C_{18}H_{34}O_{17} = 3(C_6H_{10}O_5) + 2H_2O$.

The following general analysis of yeast is the result of the author's experiments:—

Cellulose with vegetable mucus (forming the cell membranes)	37	per cent.
Protein bodies—		
(*a.*) Ordinary albumen	36	,,
(*b.*) Easily decomposed, gluten-like protein	9	
Peptones precipitable by lead acetate	2	
Fat	5	
Ash	7	
Extractive matters	4	
	100	,,

The 4 per cent. of extractive is composed of a *peptone-like* body, traces of *invertin*, *leucine* and *grape-sugar*, smaller traces of *glycerin*, *succinic acid*, *cholesterin*, *guanine*, *xanthine*, *sarcine*, and probably *inosite* and *alcohol*.

Younger yeast differs from older in containing a larger amount of albuminates and ash, whilst the older specimens contain more cellulose and fat.

By treating yeast with 95 per cent. alcohol for two days, and then digesting at 60—65° for a few hours, the following substances were extracted, viz.: *Peptone*, *succinic acid*, *leucine*, *grape-sugar*, *glycerin*, and an *albuminate* soluble in alcohol.

By digesting with ether, *cholesterin* was obtained in solution, but *no trace of any carbon compound containing phosphorus.*[*]

The author was unsuccessful in an attempt to prepare Hoppe-Seyler's "*nucleïn*," although he exactly followed the process described in Hoppe-Seyler's *Handbuch der Physiologisch. Chem. Analyse* (p. 263): he obtained only ordinary albumin with a small admixture of calcium and magnesium phosphates.

Cellulose was prepared from yeast germs by heating with tolerably concentrated warm hydrochloric acid and then with potash; cellulose was also prepared from *mycoderma aceti* by the same process. The former cellulose is altogether insoluble in an ammoniacal solution of copper oxide, and is readily attacked by concentrated nitric acid, whilst the latter is but slowly acted on by this acid even when hot, but is dissolved by ammoniacal copper oxide solution.

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[*] Hoppe-Seyler (*Med. Chem. Untersuchungen*, Heft 4, p. 500) states that *lecithin* is extracted from yeast by the action of ether.

In the ordinarily adopted method for determining fat in yeast the cells are acted on by ether: the author regards this process as ineffectual inasmuch as the cell membranes are difficult to destroy. He has devised the following method for fat estimation: 2 to 3 grams of the yeast dried at 100° are evaporated on the water-bath with concentrated hydrochloric acid; the process is repeated several times; the mass is washed with water, warmed with absolute alcohol, which is removed by filtration, and digested with ether. The alcoholic and ethereal liquids are mixed and distilled to dryness, the residue is dissolved in chloroform, and the liquid filtered into a weighed flask from which the chloroform is distilled: the residue is then weighed as free fatty acid. The main portion of the fat thus obtained from yeast consists of oleic acid. M. M. P. M.

Fermentation of Beer. By P. MULLER (*Bull. Soc. Chim.* [2], xxix, 552).—Ordinary yeast sometimes contains ferments which continue to act after the ordinary process of fermentation has ceased. One of these called by Pasteur "green acid ferment," appears as minute spheres united together in fours, and imparts to beer a disagreeable taste. Another is *saccharomyces exiguus*, which renders the beer turbid, and imparts to it a greenish colour, and makes it "flat." It appears under the microscope as small cells in groups of from 30—50.

L. T. O.'S.

The Absorptive Power of Soils for Bases. By H. P. ARMSBY (*Landw. Versuchs.-Stat.*, xxi, 397—405).—It is held by some investigators that this absorption is due to chemical action mainly, whilst others contend for the physical nature of the action. The state of concentration and volume of the solution employed have great influence on the amount of base absorbed.

Pillitz obtained (*Fres. Zeit.*, xiv, 55 and 282) constant results by passing solutions through tubes charged with earth. He found the absorption to be proportional to the weight of soil taken, and that with a certain concentration, a maximum "saturation point" was reached which could not be passed; but he admitted that the most dilute solution was not completely exhausted, as it ought to have been if the variation usually obtained had been due to want of absorbing material.

The author experimented on the absorptive power of pure hydrated silicates, and obtained variable results, similar to those obtained by Knop (*Zeit. Anal. Chem.*, xiv, 246) for soils (of which two were employed, viz., Nile sediment and a clay soil from the neighbourhood of Leipsig). There is thus no reason for supposing that these silicates are not the principal agents in the absorption of bases by soils. The results can be explained by Gladstone's researches on the partial decomposition of salts. The author concludes that—

1. The absorption of bases by soils arises from an exchange of these bases between the hydrated silicate of the soil and the salt employed.

2. This exchange, which is a chemical process, is not complete, and its amount depends on—

a. The concentration of the solution employed;

b. The relation between the volume of the solution and the weight of soil.

3. The cause of this relation is the tendency of the substances formed to reproduce the original compounds, and the actual absorption shows the point where these two decompositions are in equilibrium.

J. T.

Analytical Chemistry.

Colorimeter for Determining the Colour Intensity of Liquids. By R. GÜNSBERG (*Dingl. polyt. J.*, ccxxviii, 457—459).

Estimation of Ammonia by Sodium Hypobromite. By M. HÖNIG (*Wien. Akad. Ber.*, 1877, lxxvi, 448—454).—Some time ago Hüfner (*Jour. pr. Chem.* [2], iii, 7) proposed a modification of Knop's (*Zeit. f. Anal. Chem.*, ix, 225) method of estimating ammonia by sodium hypobromite, which consisted in accelerating the reaction by the application of heat. As Hüfner's method, however, was applicable only to the determination of urea, the author in the present paper describes a modification of the process, so that it may be used in all cases for the estimation of ammonia, whilst the duration of the operation is reduced to a minimum.

The apparatus is of two different forms, according as the action of the sodium hypobromite causes the evolution of the nitrogen of the ammonia only, or of oxygen, and nitrogen other than that from ammonia, as in the presence of Fe, Ni, Co, HCNS, &c.

For a description of the apparatus and the method of working it, reference must be made to the original paper. Suffice it to say that it gives results which are somewhat too high, owing to the excess of sodium hypobromite itself giving off traces of oxygen on boiling; the error due to this source, however, is so small (as shown by direct experiment) that for all practical purposes it may be neglected. T. C.

Detection of Nitric Acid in Commercial Lemon-Juice. By F. D. SCRIBANI (*Gazzetta chimica italiana*, viii, 284).—This acid, which has recently come into use as an adulterant of lemon-juice, to increase its acidity, converts the citric acid of the juice, wholly or partially, during the process of concentration by heat, into oxalic, acetic, and carbonic acids, so that, on neutralising the juice with milk of lime, there is obtained, instead of citrate, a mixture of oxalate, acetate, and carbonate of calcium. To detect the nitric acid, add to a small quantity of the juice in a test-tube, an aqueous solution of ferrous chloride strongly acidulated with pure hydrochloric acid and quite free from ferric salt; boil the liquid for a few minutes; and test it with potassium thiocyanate dissolved in water. If the liquid contains nitric acid, it will be coloured more or less deeply red, according to the quantity of ferric thiocyanate thus produced.

This process succeeds equally well if the juice likewise contains common salt, sulphuric or tartaric acid, or either of these substances alone. To apply it to boiled lemon-juice, the juice must be diluted with water, to facilitate the observation of the colour produced by the thiocyanate. H. W.

Analysis of Silicates. By G. Bong (*Dingl. polyt. J.*, ccxxvii, 475; *Bull. Soc. Chim.*, 1878, xxix, 50).—To render silicates soluble, they are fused with three times their weight of minium, which may be done in a platinum crucible if organic bodies are absent. After cooling, the fused mass is dissolved in nitric acid, evaporated to dryness, and taken up with a small quantity of nitric acid and water; the silica is left undissolved. After separation of the lead by sulphuric acid or hydrogen sulphide, the filtrate contains all the constituents of the silicate excepting the silicic acid already separated. D. B.

Detection of Alum in Flour. By A. Dupré (*Analyst*, 1878, 283—285).—It is stated that, although, in alum, three constituents, viz., the potash or ammonia, the sulphuric acid, and the alumina, might be made use of for estimating the amount of alum present in a mixture, these three constituents are not by any means equally available for detecting alum in flour. The potash is entirely unavailable, on account of the large quantity present in wheat flour. This is also the case with ammonia, pure flour apparently containing a proportion of ammonia so great, that it masked the small additional quantity added in alum. The difficulty in getting the sulphuric acid into a solution available for quantitative analysis is so great, that the author as yet has not obtained any satisfactory data by estimating the sulphuric acid in alum. The alumina can be estimated both with ease and exactness. It is sometimes affirmed that, inasmuch as millstones are not only frequently repaired with a cement containing alum, but are also soaked in a solution of alum, small quantities of alum found in flour might be derived from such sources. However, only minute traces could thus get in flour. The soil, which contains silicate of alumina and iron in somewhat varying proportions, but always with a great preponderance of silica, may adhere to the grain, and thus get mixed in flour. Pure flour, however, contains little or no silica.

The author has made an attempt to separate the alum as such, by shaking the flour up with chloroform, and allowing the mixture to stand for 24 hours. At the end of that time all the flour floats at the surface of the chloroform, whilst a small quantity of deposit is found at the bottom, containing the mineral impurities, and among them the alum. By using a flour mixed with 15 grains of finely powdered ammonia-alum to the 4-lb., the author had no difficulty in thus detecting an appreciable amount of alum in the deposit. D. B.

Volumetric Estimation of Arsenic. By A. Millot and Maquenne (*Compt. rend.*, lxxxvi, 1404).—The precipitation of arsenic as ammonium-magnesium arsenate is rarely complete, even when a large excess of magnesium salt is present. The concentrated filtrate will frequently yield arsenious sulphide when acidified, and mixed with hydrogen sulphide solution. This method is also inconvenient, because the precipitate cannot be ignited, but must be weighed on a dried filter.

The authors have employed the uranium acetate method, already applied volumetrically to the estimation of phosphoric acid. In a boiling solution, which is neutral or slightly acid with acetic acid, arsenic acid is entirely precipitated by uranium acetate, the end of the process being detected by the brown tint given to a drop of potassium ferrocyanide solution by a slight excess of the uranium acetate. The uranium solution is standardised by titration against a known quantity of arsenic acid; it is made by dissolving 20 grams of uranium acetate in a litre, and each c. c. will precipitate about 5 milligrams of arsenic acid. The solution is more dilute than that employed for phosphoric acid, on account of the higher equivalent of arsenic acid. The solution of potassium ferrocyanide must be freshly prepared to be free from colour.

The arsenic acid must be separated from all bases which would yield with it compounds insoluble in weak acetic acid. This is easily secured by passing the hydrogen arsenide from Marsh's apparatus into pure fuming nitric acid. After two hours the arsenic is usually all volatilised, as is proved by the hydrogen flame giving no arsenic stain. It is then only necessary to evaporate the acid liquid to dryness, dissolve the residual arsenic acid in water, and add 10 c.c. of sodium acetate solution, then titrate with uranium solution. Antimony, if present, is left undissolved on taking up the residue of evaporation with water, and does not interfere with the estimation. The process is rapid and exact; it has been employed by the authors in the analysis of mineral waters. F. C.

Electrolytic Method of Estimating Mercury. By F. W. CLARKE (*Deut. Chem. Ges. Ber.*, xi, 1409—1411).—The author proposes to determine mercury as follows:—The solution of the mercury compound is poured into a platinum dish, and slightly acidified with sulphuric acid; the dish is connected with the zinc end of a dichromate battery of six cells, whilst to the carbon end is attached a piece of platinum foil, which dips in the solution. At first mercurous chloride separates out, which is finally changed to metal; in the course of an hour all the mercury is precipitated. The metal thus obtained is washed carefully with acidified water, then with pure water, alcohol, and ether, and dried over sulphuric acid and weighed. Two determinations in mercuric chloride gave 73·76 per cent. and 73·85 per cent. mercury, the calculated percentage being 73·8 per cent. The method has been tried with other salts than the chloride, and is found to act in the case of insoluble basic salts. P. P. B.

Combustion of the Volatile Petroleum Hydrocarbons in Oxygen. By R. GÜNSBERG (*Dingl. polyt. J.*, ccxxviii, 454—457).—In making combustion analyses of the distillation-products from petroleum-benzin, the author employed Kopfer's method, which is based on the combustion of the hydrocarbons in oxygen by the aid of platinised asbestos. Although satisfactory results were obtained when other volatile bodies were analysed, such as absolute alcohol, yet with the volatile hydrocarbons of petroleum the process was not successful. The author attributes this failure to the limited supply of oxygen. He performed the combustion in a tube filled with copper oxide. The substance is not weighed in a sealed tube, as proposed by Kopfer, but in a small **U**-shaped tube, which remains outside the combustion-tube during the whole operation. The latter tube is open at both ends, and is filled with 70 cm. granular oxide of copper, both ends being plugged up with asbestos. At one end of the tube the absorption apparatus is fixed, while at the front end a layer of asbestos 6 cm. long is put behind the asbestos plug. The hinder part to which the absorption apparatus is attached rests in a sheet-iron channel, while the front part is free. The hydrocarbon under investigation is weighed in the small **U**-tube, made of thermometer tubing, having a well-fitting Geissler stopcock at each end. One end is fastened to the combustion-tube, the other to the gasometers supplying oxygen and air. Having heated the end portion of the tube to faint redness, the stopcock of the **U**-tube next to the combustion tube is opened, and the liquid heated, until all of it has distilled into the combustion tube. It is very important to keep the front of the latter cold enough to condense the vapours as they pass over. The cock in connection with the oxygen-receiver is now opened very gently, and a moderate stream of gas introduced (not more than one bubble per second). The combustion is then proceeded with in the usual way; the results obtained are very accurate. D. B.

A New Method for Estimating Carbon Dioxide in Mineral Waters. By W. Borchers (*J. pr. Chem.* [2], xvii, 353—371).—The author's apparatus is a modified form of that of Classen (*Zeitschr. f. Anal. Chem.*, xv, 288). The water under examination is placed in a conical flask (the diameter of which is small compared with its height), which is connected with an upright condenser, having a wide inner tube narrowed at both ends, and with a safety funnel the mouthpiece of which is connected by caoutchouc tubing with the main portion of the funnel. A tube connects the upper end of the upright condenser with a **U**-tube containing glass beads moistened with strong sulphuric acid; this tube is connected with a small calcium chloride **U**-tube, which is succeeded by a Geissler's potash bulb, after which comes a small **U**-tube, containing soda-lime or solid caustic potash; between the last-mentioned tube and an aspirator is interposed a small tube containing calcium chloride. The first calcium chloride tube, the potash bulbs, and the **U**-tube containing soda-lime are weighed before and after the operation. 300 c.c. of water was usually taken for each determination. The water is gently boiled until the potash begins to suck back in the bulbs; 2 or 3 litres of air free from carbon dioxide are then passed through the apparatus, the water being heated nearly to boiling; the water is then again briskly boiled; air is again passed through; and this process is repeated several times. The greater the quantity of alkaline bicarbonate present, the greater the length of time required for driving out the whole of the carbon dioxide. The increase in the weight of the weighed portion of the apparatus is noted as free carbon dioxide, plus that combined to form bicarbonates.

Hydrochloric acid is then passed into the flask, and the foregoing process is repeated; the combined carbon dioxide is thus obtained. Carbon dioxide may be determined in water free from salts in a much shorter time than in the case of mineral waters. The process must be modified if sulphuretted hydrogen is present. M. M. P. M.

Detection of Cotton in Linen Stuffs. By BÖTTGER (*Dingl. polyt. J.*, ccxxviii, 477). The linen stuffs should be dipped into an alcoholic solution of rosolic acid, then into a concentrated solution of sodium carbonate, and finally washed with water. The linen fibre assumes a pink colour, whilst the cotton fibre remains unaltered.

D. B.

Volumetric Determination of Phenol. By P. DEGENER (*J. pr. Chem.* [2], xvii, 390—394).—The process is based upon the reaction between bromine in aqueous solution, and phenol likewise dissolved in water, viz.:—

$$C_6H_5.OH + 3Br_2 = C_6H_2Br_3.OH + 3HBr.$$

The bromine-water employed is run into the aqueous solution of phenol, with constant shaking, so long as a precipitate of tribromophenol is produced, and until the liquid above the precipitate is perfectly clear. The slightest excess of bromine is detected by the yellowish colour which it imparts to the liquid, or by testing with potassium iodide and starch paper. The strength of the bromine-water employed must be determined by titration immediately before use. Not less than 10 c.c. and (unless the liquid be very dilute) not more than 30 c.c. of phenol solution should be employed. M. M. P. M.

Estimation of Tannin in Tea. By J. M. EDER (*Dingl. polyt. J.*, ccxxix, 81—88).—On account of the many adulterations to which tea is often subjected, it has been proposed to determine the amount of tannin present. A product of spent tea-leaves prepared to resemble Chinese tea is either sent into the market as tea, or mixed in large quantities with genuine tea-leaves. The author made it his object to examine various kinds of Chinese tea. He worked with a standard solution of gelatin, and found that, even by the addition of alum or of sal-ammoniac, the precipitation is not facilitated enough to give accurate results. Much time is needed for the separation of the deposit, a turbid liquid being obtained, which renders it difficult to distinguish the end of the reaction. Hammer's method, which depends on the determination of the specific gravity of the decoction before and after treatment with animal skin was tried, but gave unsatisfactory results, as the concentrated tea-decoction becomes turbid on cooling, and theïne tannate separates—a reaction which interferes with the determination of the specific gravity. Fleck's method of complete precipitation of tannic acid by means of acetate of copper gave good results, when the tannate of copper precipitate was collected on a filter and the copper determined. This chemist, however, proposes to treat the solution containing the tannin with an excess of acetate of copper, the quantity of which is known, and to determine the excess of copper in the filtrate by titration with potassium cyanide. In this case the solutions assume very dark colours, and it is difficult to notice the end of the reaction (potassium ferrocyanide as indicator). It is better to titrate back with sodium sulphide. The author, after drying the copper precipitate, ignites the latter in a closed crucible with sulphur in a stream of hydrogen, and calculates the percentage of tannin from the quantity of copper found. The results are within 0·2 to 0·3 per cent. of the truth. Allen has recently published a method which is based on the fact, that the precipitation of the astringent substances by means of acetate of lead is so perfect, that after the addition of a solution of potassium ferricyanide dissolved in equal parts of ammonia and water, no coloration is obtained, whilst a drop of this reagent in presence of ·01 milligram tannin still produces a distinct red coloration. The presence of pectin and of similar substances often gives high results. These substances are easily separated by means of alcohol previous to the copper precipitation.

In conclusion, it is mentioned that Fleck's separation of tannate and gallate of copper by means of ammonium carbonate, which is said to dissolve the latter, is quite useless, since the author has found that pure tannate of copper dissolves largely in ammonium carbonate.

D. B.

Technical Chemistry.

Carbon-paper rendered Sensitive without a Chrome-bath. By MONCKHOVEN (*Ding. polyt. J.*, ccxxviii, 476).—Ordinary carbon-paper is dipped into a 20 per cent. aqueous solution of citrate of iron and ammonium, and dried in a dark place. It is then exposed to the light in the copying frame, moistened, and brought on the glass plate. On developing with warm water, no picture is visible. However, if after exposure to the light, the paper is dipped into a solution of potassium dichromate instead of water, and then brought on the glass plate and developed with warm water, a picture is obtained, the action of the light being transferred from the iron salts to the chromium salt. Mercuric chloride or other salts may be used in the place of the chromium salt. If tannin is used, the action of the light is reversed, and a negative picture is obtained. Instead of iron salts, other metallic salts, the bases of which are capable of various degrees of oxidation, may be employed. In this process there is great difficulty in obtaining the half-tones. D. B.

Kisjak, a Fuel used in the South of Russia. By C. O. CECH (*Dingl. polyt. J.*, ccxxviii, 468—470).—This fuel is prepared from well-seasoned horse- and cattle-dung, by spreading it out in a thin layer, treating with water, and kneading the moist mass to a well-mixed dough. The mixture is then formed into bricks in wooden moulds and dried. It is largely used in the southern parts of Russia as a substitute for wood, there being but few forests in that portion of the country. The following analyses give the value of turf made from horse- and sheep-dung:—

	C.	H.	O.	N.	Salts and earthy substances.
Horse-dung bricks	41·386	4·985	33·396	1·703	18·530=100·000
Sheep-dung „	28·690	3·785	27·990	1·907	37·630=100·002

Kisjak becomes red hot very slowly. An ordinary oven is charged with about 20 of the bricks, the latter being lighted with a few pieces of wood. In windy weather this fuel evolves disagreeably-smelling gases; it is therefore used only for heating baths, wash-houses, or in the rooms of the poorer classes of people. D. B.

Purification and Analysis of Water. By E. Bohlig (*Arch. Pharm.* [3], xiii, 14—23).—According to the arguments and analysis brought forward, calcium carbonate in spring waters does not exist as the bicarbonate, this latter body having no existence. Hydrated magnesium oxide is recommended as the best purifier of hard waters, the calcium carbonate being completely precipitated. E. W. P.

Purification of Water containing Magnesia. By R. Günsberg (*Dingl. polyt. J.*, ccxxviii, 450—454).—The author had occasion to analyse some water obtained from Jassy, which is very largely used, and contains more magnesia than lime. He also investigated the degree of purification by Bohlig's magnesia-preparation. The following observations were made:—

(1.) By adding lime to the water (Clark), magnesium carbonate is not separated completely at the ordinary temperature, boiling being necessary. From a pure solution of magnesium bicarbonate, nearly all magnesia is separated as carbonate by long-continued boiling. In the presence of alkaline salts, the separation is not complete; apparently a reaction takes place between the magnesium and alkaline salts, resulting in the formation of an alkaline carbonate.

(2.) With soluble lime salts and also with gypsum (de Haën), magnesium carbonate is completely decomposed only on boiling, provided that the solvent for the corresponding lime salt is not diminished, so as to cause the possible separation of this salt. In this case if a sufficient quantity of magnesium carbonate is present, all the lime will be separated as carbonate on long-continued boiling.

(3.) By adding magnesium hydrate to the water and boiling it (Bohlig), magnesium carbonate is separated completely if alkalis and soluble lime salts are absent. The decomposition of magnesium carbonate, in presence of soluble lime salts, is effected very readily at the boiling point. If magnesia is added, without the addition of the latter, continued boiling is necessary.

(4.) By the addition of sodium carbonate, magnesium salts are not separated completely (Berenger, Stingl, and Schulz).

It will be seen from the above that Bohlig's purification method is the most suitable of all. Clark's method may be applied to this water if, after the addition of the corresponding quantity of lime, the water is boiled, in which case magnesium salts separate as magnesia, the lime being removed by a corresponding quantity of sodium carbonate, and the operation completed in the usual manner. D. B.

Analysis of Refractory Materials. By G. J. SNELUS (*Dingl. polyt. J.*, ccxxviii, 475).—

Name of Material.	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Alkalis.
Patent Glenboig-stones..	62·00	34·00	2·70	—	traces	—[1]
Dowlais-clay	67·49	27·05	1·99	0·43	0·94	1·43[2]
Ditto	69·53	23·37	1·67	0·37	0·65	1·13[3]
Newcastle-stone........	60·53	33·28	2·61	0·47	0·64	2·53
Ditto	58·00	36·50	1·67	0·50	0·90	2·42
Ditto	55·67	38·87	1·67	0·58	0·82	2·12
Ditto	63·82	31·68	1·63	0·48	0·70	2·03
Stourbridge-stone	69·50	27·52	1·90	0·32	0·10	—
Dinas- (silica) stone	96·58	2·43	—	1·01	—	—[4]
St. Helen's-stone	63·80	31·00	2·80	0·60	0·75	1·05
Bauxill-clay	4·12	53·62	42·26	—	—	—
Silica-stone............	95·53	3·26	—	0·99	0·42	—[5]
Ditto	97·50	1·70	—	0·55	0·22	—[6]
Ditto	95·60	3·22	—	0·97	—	—[7]
Ditto	95·48	3·44	—	1·02	0·20	—[8]
Ditto	95·51	2·90	—	1·08	—	—[9]
Ditto	95·64	3·72	—	0·95	—	—[10]
Sheffield-ganister	95·55	4·85	0·85	0·60	0·11	0·94[11]
Dowlais-ganister	93·50	4·23	0·80	0·26	traces	—[12]

D. B.

Burning of Bricks in Annular Kilns. By F. FISCHER (*Dingl. polyt. J.*, ccxxviii, 432—442).—A large quantity of calcium carbonate present in clay used for the manufacture of bricks is known to be injurious. Although such clays are easily worked up, they lose when heated not merely water, but carbonic acid, and result in the formation of a porous mass, from which clinker can be prepared only with difficulty. To conduct the operation in a manner which will give a satisfactory product is an extremely difficult task, as these clays do not stand the fire, *i.e.*, the temperature at which softening and formation of a porcelaineous compact mass takes place is near that at which complete fusion to a slag sets in. It is therefore necessary not to heat too strongly, in order to retain the porous and earthy fracture of the stone. The products thus obtained are much used in the northern part of Germany for facing houses. The colour is often yellow or yellowish-green, owing to the formation of a yellow basic silicate of calcium and iron. While moderately pure clay forms a white product, the sulphates of magnesium, calcium, and sodium, or sodium chloride and bicarbonate, form, after exposure, white, yellow, green, or even black blotches. Algæ and fungi often form green or black spots. The colour of bricks is also influenced by the composition of the flue gases. Excess of oxygen colours clay containing iron and lime, red, yellow, or brown. Reducing gases (hydrogen, hydrocarbons, carbonic oxide) form black colours. Clay with iron alone assumes a red colour in oxygen, whilst reducing gases change it to a satiny-black colour.

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[1] This stone is coloured red with black spots. It is very hard and strong, and is much used for Siemens' furnaces. It resists the heat of a welding furnace for more than twelve months.

[2] and [3] are used for puddling works; they are, however, not very durable, as they only resist the heat of welding furnaces for one month.

[4] This stone lasted for a long time. [5] Badly. [6] Very good.

[7] Badly. [8] Lasts very badly. [9] Moderately well.

[11] A black coloured ganister which sets easily.

[12] If used for moulds it is merely ground up without any admixture.

In this paper analyses of the flue-gases of two kilos. are given. It is shown from these that carbonic oxide is not present, complete combustion taking place. Since reducing gases cannot be formed in annular-kilns, it becomes a delicate operation to turn out bricks for facings having a pure and white colour. D. B.

Influence of Chemically-combined Carbon on the Hardness of Iron. (*Dingl. polyt. J.*, ccxxviii, 474).—Charcoal cold-blast pig iron is said to yield the best chilled product, but this has never been fully investigated. Gill has analysed some iron carriage wheels, the durability of which had been determined practically. It was shown that hot-blast pig iron contained a larger percentage of silicon than cold-blast iron, and that the percentage of chemically-combined carbon goes hand in hand with silicon, inasmuch as the percentage of the latter is in the inverse ratio to that of the carbon. From this it is concluded that the property which foundry-iron possesses of being hardened depends on the chemically-combined carbon, and that the hardness increases or decreases with the latter. D. B.

Mill-dust and a Coloured Alga present in Flour. By B. JEGEL (*Dingl. polyt. J.*, ccxxviii, 476—477).—The following figures give an account of the quantity of millstone dust present in commercial flour. The amount was determined by Himly's method of shaking up 100 grams of the flour with chloroform in a separating funnel. The deposit was transferred to a weighed dish, washed with ether by decantation, dried, ignited and weighed. 100 parts of four different qualities of rye-flour contained:—

	I.	II.	III.	IV.
Mill-dust......	0·02	0·04	0·14	0·158
Ash..........	0·80	0·80	1·02	1·33
Moisture......	14·70	15·862	15·02	14·484

In examining these qualities with chloroform it was found that a light blue solid layer had been deposited on the dark-coloured dust; this mass was investigated microscopically, and proved to consist of a series of round cells, having a diameter of 0·002 to 0·004 mm. The light blue colour of this alga was changed to light red by acids; alkalis gave a yellowish-green colour. D. B.

Sulphuric Saponification. By E. FRÉMY (*Compt. rend.*, lxxxvii, 5—7).—Many years ago the author, in laboratory experiments, obtained the acid constituents of neutral fats as white solids, by heating the fats with sulphuric acid, decomposing the resulting sulpho-acid by long ebullition, and submitting the separated fat-acids to pressure, His process has since been applied to industrial operations with complete success, and the present Paris Exhibition contains specimens of perfectly white solid fat-acids, which have been obtained without distillation by means of sulphuric saponification. R. R.

The Composition and Properties of Wood Gunpowders. By F. Woodland Toms (*The Field*, 1878, No. 1,336, p. 143).—The author reports the result of analyses of samples of wood gunpowders made in connection with a practical trial of explosives for the purpose of ascertaining the relative advantages for sporting purposes of the Schulze or wood gunpowder, and the ordinary or black gunpowder. The three samples selected for analysis were those whose explosive effect, penetration, recoil, &c., had been previously determined by the editor of *The Field*. One was a sample of ordinary powder supplied by the Schulze Company in 1877, a second was a sample from a batch previously issued and recalled, owing to its violent action, which had caused damage to several guns; and the third was a more carefully prepared sample (although less regular in strength than that of the previous year made this season), and used at the competition arranged by the editor of *The Field* between the different makers of black gunpowders and the Schulze Company.

The analysis shows that the wood powder consists of a mixture of explosive and non-explosive nitro-cellulose, obtained by the action of nitric and sulphuric acid upon prepared wood fibre, and that this converted wood fibre is further impregnated with a mixture of potassium and barium nitrates. The extreme explosive force of the dangerous sample is traced to its containing a larger proportion of explosive nitro-cellulose (the tri-nitro-cellulose or gun-cotton) and to its being of a greater density than the other powders. The author further points out that the first two samples did not come up to the Government test of stability (the 10 minutes' heat test), whilst the powder now manufactured was well over the limit; this he shows is due to greater care being exercised in preparing the wood fibre, and in washing the product so as to free it from acid. C. E. G.

Insoluble Gum for Envelopes, &c. By A. C. Fox. (*Dingl. polyt. J.*, ccxxviii, 478).—This consists of two distinct preparations. That part of the envelope which is covered by the flap, and not touched by the lips or tongue, is coated with a solution consisting of 2·5 grams of crystallised chromic acid in 15 grams of water and 15 grams of ammonia; to this solution about 10 drops of sulphuric acid are added, and finally 30 grams of sulphate of copper and ammonium, and 4 grams of fine white paper. The inside of the flap is coated with a solution prepared by dissolving isinglass in dilute acetic acid (1 part acid to 7 parts water) on the water-bath. When the envelope has been fastened, the moistened isinglass on the inside of the flap comes in contact with the chromium preparation on that portion of the envelope covered by the flap, and a solid cement is produced by the action of the two preparations; this is perfectly insoluble in acids or alkalis, in hot or cold water, and in steam. D. B.

On Galleïn and Coruleïn. By Durant (*Dingl. polyt. J.*, ccxxix, 178).—In the *Bulletin de la Société industrielle de Mulhouse*, 1878, 326, the author gives an account of the preparation of these substances on a large scale:—1 pt. of phthalic acid is heated with 2 pts. of pyrogallic acid at 190° to 200° until the mass becomes hard. It is then exhausted with boiling water, whereby a certain residue of unaltered pyrogallic and phthalic acids is removed; the residue is then dissolved with alkaline carbonates, and the solution precipitated by acids. The galleïn obtained is insoluble in cold water, sparingly soluble in hot water, and easily soluble in hot alcohol. Its concentrated alcoholic solution shows a mahogany-yellow coloration. Its alkaline solution is coloured bluish-violet, but this disappears rapidly on exposure to the air, the solution forming brown-coloured products. Coruleïn is obtained by heating 1 pt. of dry galleïn with 20 pts. of sulphuric acid at 200°, the mass when cold being poured into water, and the adhering acid removed by washing. Coruleïn is not attacked by acids or alkalis, and therefore corresponds with all the demands of a fast colouring matter. Galleïn gives compounds with various metallic oxides; with lead mordants a very fine grey-violet is obtained, but chromic oxide forms the most important and useful mordant, and gives the finest shades.

For printing on oiled cotton 40 litres of galleïn paste are mixed with 20 litres of gum-water, and to the whole 4 litres acetate of chromium of 1·1415 sp. gr. added; the printed goods are then steamed, washed, and soaped. Both cotton and wool may be dyed with galleïn after previously mordanting with chromium. The operation is similar to the dyeing with alizarin. In printing or dyeing with coruleïn the latter is dissolved in sodium thiosulphate. For printing on wool 10 litres of coruleïn are thickened with 30 litres of gum-water, treated with 2·5 litres of glycerin, and, immediately before use, 1·25 litre of a solution of sodium thiosulphate is added (sp. gr. 1·3804). For cotton prints on oiled cloth 8 litres coruleïn, 20 litres gum-water, 2 litres acetate of chromium (1·1415 sp. gr.), and 1 litre sodium thiosulphate (of the above strength and immediately before use) are taken. Kochlin recommends the use of potassium ferrocyanide as mordant (250 grams to 1 litre coruleïn). For dyeing with coruleïn the same conditions answer, with the exception that 1 kilo. coruleïn must be dissolved previously in 2 kilos. sodium thiosulphate of 1·3804 sp. gr. All colours obtained with the latter colouring matter are very fast. It may, like indigo, be reduced on tissues re-oxidised in the air. Zinc-dust in presence of ammonia forms the best reducing agent.

D. B.

General and Physical Chemistry.

Absorption-Spectra of certain Colouring Matters in Various Solvents. By F. v. Lepel (*Deut. Chem. Ges. Ber.*, xi, 1146—1151). —The author in a great number of cases confirms Kundt's law (*Pogg. Ann.*, 615), that the absorption-band of a colouring matter moves the nearer to the red end the greater the refractive index of the solvent. With some, however, an increase in the refractive index of the solvent does not produce any alteration in the spectrum, whilst with others a movement of the band towards the violet, or a complete change in its character, ensues. Vogel's explanation (*Ber.* xi, 623) of these exceptions is adopted, viz., that it is not likely that the characteristic absorption-spectra of a colouring matter can be observed under all circumstances.

The spectra of the following dyes are described, a diagram being given in each case:—Saffranin, kermes, methyl-violet, eosin, Guernsey blue, dahlia, cochineal, Brazil wood, logwood, sandalwood, turmeric, and alizarin, the solvents employed being water, ether, alcohol, chloroform, and carbon bisulphide, arranged according to increasing refractive index; also ammonia and acetic acid. The layers of the solutions used were of equal thickness, and in the case of the same colouring matter, of equal colour intensity. When the dye was insoluble in any of the above solvents, solution was obtained by the addition of a little absolute alcohol.

Saffranin.—The aqueous solution gave a band between D and *b*, becoming very faint towards F. With other solvents, there was a band only at E, the maximum being nearer D with ether, chloroform, and carbon bisulphide than with alcohol. Ammonia and acetic acid produce spectra similar to that with water.

Kermes.—The aqueous solution showed only one band at E, whilst the other solvents gave two, which obey Kundt's law. Acetic acid and ammonia produced bands almost similar, the maximum of the latter being towards E, and that of the former towards *b*.

Methyl-violet does not obey Kundt's law. All the solutions give a similar band, with a maximum between D and E.

Eosin with water showed one band at *b*, while with the other solvents it gave two, of which the darker was at E, and the other between *b* and F.

Guernsey Blue and Dahlia gave in all solvents a single band at D.

Cochineal.—The band given by an aqueous solution at *b*, became much weaker with other solvents, ether causing it to disappear altogether; with chloroform it spreads out on both sides beyond F and *b*. The band on the violet side of D had its maximum nearer to D with alcohol than with ether and chloroform. Acetic acid caused the bands at D and *b* to run into one another, while at the same time absorption occurred at G.

Brazil wood and Logwood.—These are already known, and do not need description.

Sandalwood.—The straw-yellow alcoholic liquid, diluted with alcohol, chloroform, or carbon bisulphide, gave one band at $\frac{b}{2}$F, and a second close on F, running on towards G; at the last point another slight absorption appeared. The strong aqueous solution gave similar bands, but displaced towards the red. By transmitted light, the solution was rose-coloured, and by reflected light, a muddy orange. The ethereal solution, which is bright yellow by transmitted, and green by reflected light, gave one absorption-band at $\frac{b}{2}$F, and two between F and G. The acetic acid solution gave only one band at *b*, spreading out faintly beyond F. The ammoniacal solution produced a continuous band from D to beyond G, showing however two maxima at E and F.

Turmeric does not obey Kundt's law. It exhibited a continuous absorption with ether, alcohol, chloroform, carbon bisulphide, and acetic acid, beginning with alcohol at $\frac{b}{2}$F, and with the others at F. The ammoniacal solution gave one band at F.

Alizarin.—With *much* water it produced an absorption between D and F, showing two maxima, one between D and E, and the other between *b* and F. In all other cases, except where ammonia was used, there was no absorption until just on the red side of F, which began somewhat nearer *b* with alcohol than with the other solvents. If, however, *little* water be present, there occurs a very considerable absorption between D and E, except in the case of carbon bisulphide, with which this phenomena was not observed. Acetic acid had no effect on the spectrum. Ammonia with sufficient dilution produced the well known violet coloration and three bands, at C, D, and F.* Addition of water caused the band at C to disappear. T. C.

Depolarisation of Electrodes by Metallic Solutions. By LIPPMANN (*Compt. rend.*, lxxxvi, 1540—1541).—An attempt has been made to utilise the fact of the depolarisation of an electrode by solutions of its own salts, in order to detect the presence of certain metals in solution. If, through a solution suspected to contain copper, a feeble current be passed by means of a copper negative electrode, properly connected with a mercurial capillary electrometor, the latter will show instantaneous polarisation of the electrode if copper is absent, whereas by a negative indication it will detect the $\frac{1}{5000}$th part of copper dissolved, even in presence of other metallic salts. The method is said to be still more sensitive with a silver electrode in presence of silver solution, than with copper, but the limit of the reaction has not been measured. J. W.

Law of Volumes in Solid Bodies. By H. SCHRÖDER (*Deut. Chem. Ges. Ber.*, xi, 1109—1116, and 1142—1146).—*In every solid compound the volume measure* (volummaass), *i.e., the stere, of one of its elements, which through the forces acting during crystallisation, determines all the other components and respective constituents, causes equal volume*

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* In the diagram the first band is represented at *d* and not at C.—T.C.

measures to take up equal steres. In other words, one of the elements assimilates to itself all the others.

By the use of this law the author endeavours to determine the molecular volume of a solid body, for the solid molecule contains only whole volumes or steres of each element. Thus, the solid molecules of zinc and zinc oxide are respectively Zn_3 and Zn_3O_3, because 3 atoms of zinc, both alone and in the oxide, occupy the space of 5 volume units or steres, and the 3 atoms of oxygen three steres.

The number of atoms of each element in a compound is indicated in the ordinary manner by a whole number placed to the right of the under side of the symbol, and the number of its steres by a whole number to the right of the upper side. The stere is distinguished by an over-stroke, and the observed and calculated volumes by a similar under-stroke. The element in a compound which determines the steres is also indicated by an over-stroke. Thus metallic silver is:—

$$\overline{Ag_1^2} = 2 \times \overline{5\cdot14} = \underline{10\cdot28}, \text{ observed vol.} = \underline{10\cdot28},$$

i.e., an atom or 108 grams silver occupies 10·28 c.c. = 2 × $\overline{5\cdot14}$ c.c., or two silver steres.

Again the chloride, bromide, and iodide of silver are represented thus:—

$$\overline{Ag_1^2}Cl_1^3 = 5 \times \overline{5\cdot14} = \underline{25\cdot70}, \text{ observed vol.} = \underline{25\cdot70}$$
$$\overline{Ag_1^2}Br_1^4 = 6 \times \overline{5\cdot14} = \underline{30\cdot84}, \quad ,, \quad = \underline{30\cdot84}$$
$$\overline{Ag_1^2}I_1^6 = 8 \times \overline{5\cdot14} = \underline{41\cdot12}, \quad ,, \quad = \underline{41\cdot12}$$

From this it is seen that in all three compounds the silver stere dominates.

The author has likewise previously proved the truth of the law in the case of the three following groups:—

(*a*.) *Silicon.*—Quartz, sillimanite, disthene.
(*b*.) *Aluminium.*—Corundum, chrysoberyll, diaspore, and andalusite.
(*c*.) *Magnesium.*—Periclase, spinelle, olivene, diopside, humite, and garnet. (*Ber. Akad. München*, [1877], 302.)

And also for a series of oxides (this Journal, 1877, ii, 698), and the compounds of chlorine, bromine, and iodine.

Mercury Compounds.—It has previously been shown (*Annalen*, clxxiii, 251), that mercuric chloride and bromide are isosteric with the chlorides and bromides of the other metals of the magnesium group, for mercury and most of its compounds has the same stere as the rest of the metals of the magnesium group, viz., $\overline{5\cdot52}$. The almost exact agreement of the calculated and observed molecular volume of nearly all mercury compounds, as well as of a great number of other bodies, especially the oxides of manganese (*vide infra*), is very remarkable and conclusive as to the truth of the laws of condensation, and of volumes in solid bodies. Thus:—

$$\text{Mercurous oxide} = \overline{Hg_2}O_1^2 = 7 \times \overline{5\cdot52} = \underline{38\cdot64}, \text{ observed} = \underline{38\cdot64}$$
$$\text{Mercuric} \quad ,, \quad = \overline{Hg_2}O_2^2 = 7 \times \overline{5\cdot52} = 38\cdot64 = 2 \times \underline{19\cdot32},$$
$$\text{observed} = \underline{19\cdot32}$$

Amorphous black cinnabar = $\overline{\mathrm{Hg}^{5}_{2}}\mathrm{S}^{6}_{2} = 11 \times \overline{5{\cdot}52} = 60{\cdot}72 = 2 \times \underline{30{\cdot}36}$, observed = $\underline{30{\cdot}36}$

Red rhombohedric cinnabar = $\mathrm{Hg}^{5}_{2}\overline{\mathrm{S}^{6}_{2}} = 11 \times \overline{5{\cdot}30} = 58{\cdot}3 = 2 \times \underline{29{\cdot}10}$, observed = $\underline{29{\cdot}10}$.

The black cinnabar, therefore, is distinguished from the red by the fact that in the former the mercury stere dominates, whilst in the latter it is the sulphur stere = $\overline{5{\cdot}3}$.

The mercury in its chlorides and bromides, and also in the cyanide, is present as Hg^{3}_{1}, and not as Hg^{5}_{2}. Thus:—

Mercurous chloride = $\overline{\mathrm{Hg}^{3}_{1}}\mathrm{Cl}^{3}_{1} = 6 \times \overline{5{\cdot}52} = \underline{33{\cdot}12}$, observed = $\underline{33{\cdot}12}$ (Schrœder and Boullay)

„ bromide = $\overline{\mathrm{Hg}^{3}_{1}}\mathrm{Br}^{4}_{1} = 7 \times \overline{5{\cdot}52} = \underline{38{\cdot}64}$, observed = $\underline{38{\cdot}64}$ (Schrœder and Karsten)

Mercuric chloride = $\overline{\mathrm{Hg}^{3}_{1}}\mathrm{Cl}^{6}_{2} = 9 \times \overline{5{\cdot}52} = \underline{49{\cdot}68}$, observed = $\underline{49{\cdot}68}$ (Schrœder and Boullay)

„ bromide = $\overline{\mathrm{Hg}^{3}_{1}}\mathrm{Br}^{8}_{2} = 11 \times \overline{5{\cdot}52} = \underline{60{\cdot}72}$, observed = $\underline{60{\cdot}72}$ (Schrœder and Karsten)

„ cyanide = $\overline{\mathrm{Hg}^{3}_{1}}\mathrm{Cy}^{9}_{2} = 12 \times \overline{5{\cdot}52} = \underline{66{\cdot}24}$, observed = $\underline{66{\cdot}24}$ (Bödeker).

The iodides of mercury do not give such good results as the foregoing compounds, and are still under investigation.

Manganese Oxides and Silicates.—Metallic manganese has, according to John, the volume 6·9 = $\frac{1}{2}$ vol. of Mg.

$\overline{\mathrm{Mn}^{5}_{4}} = 5 \times \overline{5{\cdot}52} = 27{\cdot}6 = 4 \times \underline{6{\cdot}90}$, observed = 6·90.

Pyrolusite = $\overline{\mathrm{Mn}^{5}_{4}}\mathrm{O}^{8}_{8} = 13 \times \overline{5{\cdot}52} = 71{\cdot}76 = 4 \times \underline{17{\cdot}94}$, observed = 17·8—18·0.

Manganite is isomorphous with göthite and diaspore. The molecular volumes of these bodies are as follows:—

Diaspore = $\overline{\mathrm{Al}^{2}_{2}}\mathrm{H}^{1}_{2}\mathrm{O}^{4}_{4} = 7 \times \overline{5{\cdot}14} = \underline{35{\cdot}98}$, observed = 35·98

Manganite = $\mathrm{Mn}^{5}_{4}\mathrm{H}^{2}_{4}\overline{\mathrm{O}^{8}_{8}} = 15 \times \overline{5{\cdot}40} = 81 = 2 \times \underline{40{\cdot}5}$, observed = $\underline{40{\cdot}5}$

Göthite = $\mathrm{Fe}^{5}_{4}\mathrm{H}^{2}_{4}\overline{\mathrm{O}^{8}_{8}} = 15 \times \overline{5{\cdot}40} = 81 = 2 \times \underline{40{\cdot}5}$, observed = $\underline{40{\cdot}5}$

In diaspore, therefore, the aluminium stere dominates, but in manganite and göthite the oxygen stere (= 5·40).

All the other oxides of manganese contain the manganese as Mn^{3}_{2}. Thus:—

Manganous oxide = $\overline{\mathrm{Mn}^{3}_{2}}\mathrm{O}^{2}_{2} = 5 \times \overline{5{\cdot}52} = 27{\cdot}60 = 2 \times \underline{13{\cdot}80}$, observed = 13·80 (Rammelsberg).

Braunite $= \overline{\mathrm{Mn}}{}^{3}_{2}\mathrm{O}^{3}_{3} = 6 \times \overline{5{\cdot}52} = \underline{33{\cdot}12}$, observed $= \underline{33{\cdot}12}$ (Rammelsberg).

Hausmannite $= \overline{\mathrm{Mn}}{}^{9}_{6}\mathrm{O}^{8}_{8} = 17 \times \overline{5{\cdot}52} = 93{\cdot}82 = 2 \times 46{\cdot}91$, observed $= 47{\cdot}10$ (Rammelsberg).

Though regular magnetic iron ore and quadratic hausmannite have a similar volume constitution, yet in the former, as in spinelle, the oxygen stere dominates, whilst in the latter it is the manganese stere.

In the manganese silicates, the manganese has the condensation Mn^{3}_{2}, and the silicic acid the same volume constitution as quartz, viz., $\mathrm{Si}^{2}_{1}\mathrm{O}^{2}_{2}$. Thus:—

Tephroite $= \mathrm{Mn}^{3}_{2}\mathrm{Si}^{2}_{1}\overline{\mathrm{O}^{4}_{4}} = 9 \times \overline{5{\cdot}4} = \underline{48{\cdot}6}$, observed $= \underline{48{\cdot}6}$

Rhodonite $= \overline{\mathrm{Mn}}{}^{21}_{14}\mathrm{Ca}^{1}_{1}\mathrm{Mg}^{1}_{1}\mathrm{Si}^{32}_{16}\mathrm{O}^{48}_{48} = 103 \times 5{\cdot}52 = \underline{596{\cdot}16}$, observed $\underline{596{\cdot}16}$ (Longban)

Fowlerite $= \overline{\mathrm{Mn}}{}^{27}_{18}\mathrm{Mg}^{2}_{2}\mathrm{Zn}^{2}_{2}\mathrm{Ca}^{4}_{4}\mathrm{Si}^{52}_{26}\mathrm{O}^{78}_{78} = 165 \times \overline{5{\cdot}52} = 910{\cdot}8 = 2 \times \underline{455{\cdot}4}$, observed $= \underline{455{\cdot}4}$ (Hermann)

Pajsbergite $= \overline{\mathrm{Mn}}{}^{6}_{4}\mathrm{Ca}^{1}_{1}\mathrm{Si}^{10}_{5}\mathrm{O}^{15}_{15} = 32 \times \overline{5{\cdot}52} = \underline{176{\cdot}64}$, observed $= \underline{176{\cdot}64}$ (Igelström).

In the first of these minerals the oxygen stere dominates, whilst in the remaining three it is the manganese stere.

Sulphides and Arsenides of Fe, Co, Ni, Cu, Zn, and Pb.—The following facts show that the arsenic stere $= \overline{5{\cdot}3}$:—

Rhombohedric arsenic $= \overline{\mathrm{As}^{5}_{2}} = 5 \times \overline{5{\cdot}3} = 26{\cdot}5 = 2 \times \underline{13{\cdot}25}$, observed vol. $= 13{\cdot}1$—$13{\cdot}2$ (Hittorf, Bettendorff, and Wüllner)

Amorphous (regular) arsenic $= \overline{\mathrm{As}^{3}_{1}} = 3 \times \overline{5{\cdot}3} = \underline{15{\cdot}9}$, observed $= \underline{15{\cdot}9}$ (Hittorf, Bettendorff, and Wüllner)

Rhombohedric arsenious oxide $= \overline{\mathrm{As}}{}^{6}_{2}\mathrm{O}^{3}_{3} = 9 \times \overline{5{\cdot}3} = 47{\cdot}7$, observed $= \underline{47{\cdot}7}$ (Groth)

Regular „ $= \overline{\mathrm{As}}{}^{5}_{2}\mathrm{O}^{5}_{3} = 10 \times \overline{5{\cdot}3} = \underline{53{\cdot}0}$, observed $= \underline{53{\cdot}0}$

Arsenic oxide $= \mathrm{As}^{5}_{2}\mathrm{O}^{5}_{5} = 10 \times \overline{5{\cdot}3} = \underline{53{\cdot}0}$, observed $= \underline{53{\cdot}0}$ (Schrœder and Filhol).

Sulphur in the monoclinic form and ordinary phosphorus have the stere $\overline{5{\cdot}4}$. Thus:—

$$\mathrm{S}^{3}_{1} = 3 \times \overline{5{\cdot}4} = \underline{16{\cdot}2}, \text{ observed } = \underline{16{\cdot}2}$$

$$\mathrm{P}^{3}_{1} = 3 \times \overline{5{\cdot}4} = \underline{16{\cdot}2}, \quad „ \quad = \underline{16{\cdot}2}.$$

In most metallic sulphides, however, the sulphur has the same stere as arsenic, and generally replaces the latter without change of volume; in a similar manner phosphorus has the same stere in phosphates that arsenic has in arsenates, viz., $\overline{5{\cdot}3}$. The greater stere of S and P in the free state is due to their volume having been observed much nearer the melting-point.

In iron pyrites and marcasite the sulphur is condensed to half its original volume, and the two minerals differ from one another only in the dominating stere, for in the former we have the sulphur stere, and in the latter the iron stere. Thus:—

Pyrites $= \mathrm{Fe}^3_2\overline{\mathrm{S}^6_4} = 9 \times \overline{5\cdot3} = 47\cdot7 = 2 \times \underline{23\cdot85}$, observed = 23·85

Marcasite $= \overline{\mathrm{Fe}^3_2}\mathrm{S}^6_4 = 9 \times \overline{5\cdot52} = 49\cdot68 = 2 \times \underline{24\cdot84}$, observed = 24·84 (Rose).

In all other sulphides and arsenides of Fe, Co, Ni, and Cu, the sulphur and arsenic each occupy two steres.

Troilite .... $= \mathrm{Fe}^3_2\overline{\mathrm{S}^4_2} = 7 \times \overline{5\cdot3} = 37\cdot1 = 2 \times \underline{18\cdot55}$, observed = 18·55 (Rose and Rammelsberg)

Ferric sulphide........ $= \mathrm{Fe}^3_2\overline{\mathrm{S}^6_3} = 9 \times \overline{5\cdot3} = 47\cdot7$, observed = $\underline{47\cdot7}$ (Rammelsberg)

Magnetic pyrites ...... $= \mathrm{Fe}^{12}_8\overline{\mathrm{S}^{18}_9} = 30 \times \overline{5\cdot3} = \underline{159\cdot0}$, observed = $\underline{159\cdot0}$ (Rose and Rammelsberg)

Leuco-pyrites (rhombic) $= \mathrm{Fe}^3_2\overline{\mathrm{As}^6_3} = 9 \times \overline{5\cdot3} = \underline{47\cdot7}$, observed = $\underline{47\cdot7}$ (Güttler)

Löllingite (rhombic) .. $= \mathrm{Fe}^3_2\overline{\mathrm{As}^8_4} = 11 \times \overline{5\cdot3} = 58\cdot3 = 2 \times \underline{29\cdot15}$, observed = 29·15 (Scheerer, Breithaupt, and Illing)

Speiscobalt (regular) .. $= \mathrm{Co}^3_2\overline{\mathrm{As}^8_4} = 11 \times \overline{5\cdot3} = 58\cdot3 = 2 \times \underline{29\cdot15}$, observed = 29·15 (Varrentrapp and Sandberger)

Tesseral pyrites (regular) $= \overline{\mathrm{Co}^3_2}\mathrm{As}^{12}_6 = 15 \times \overline{5\cdot52} = 82\cdot8 = 2 \times \underline{41\cdot4}$, observed = 41·4 (Scheerer).

The volume of arsenical pyrites = sum of the vols. of pyrites, FeS_2, and löllingite $FeAs_2$. Thus:—

$\mathrm{Fe}^3_2\overline{\mathrm{S}^3_2\mathrm{As}^4_2} = 10 \times \overline{5\cdot3} = 53\cdot0$, observed = $\underline{53\cdot0}$

White nickel pyrites $= \mathrm{Ni}^3_2\overline{\mathrm{As}^8_4} = 11 \times \overline{5\cdot3} = 58\cdot3 = 2 \times \underline{29\cdot15}$, observed = 29·15 (Breithaupt and Sandberger).

From the above volume-values of sulphides and arsenides it appears:—

1. That with the exception of tesseral pyrites, they all have equal steres, and that the following form isosteric groups:—

(*a*.) Rhombic arsenic trioxide, As_2O_3; ferric sulphide, Fe_2S_3; leuco-pyrites, Fe_2As_3; their volume being = 47·7.

(*b*.) Rhombohedric arsenic, As_4; vitreous As_2O_3; ignited As_2O_5; and arsenical pyrites, $Fe_3S_2As_2$, their volume being = 53·0.

(*c*.) White nickel pyrites $NiAs_2$; speiscobalt, $CoAs_2$; löllingite, $FeAs_2$; nickel glance, NiAsS, their volume being = 29·2.

2. The volume of compounds which contain a two-atom radicle, as

leuco-pyrites and arsenical pyrites, are directly divisible by the arsenic stere without remainder; while the remaining compounds have volumes which are likewise divisible by 5·3 without remainder, if their molecule is represented so that they contain a two-atom radicle.

3. From the fact that löllingite, $Fe_2As_4 = 58{\cdot}3$, and leuco-pyrites, $Fe_2As_3 = 44{\cdot}7$, it follows that the vol. of $As = 10{\cdot}6 = 2 \times 5{\cdot}3$, a result identical with that previously obtained.

4. From the isosterism of leuco-pyrites and ferric sulphide it follows that $S^{2}_{1} = As^{2}_{1}$.

Details are also given with regard to the following sulphides and arsenides, the molecular formulæ attached being those derived by the above method. The copper stere = $\overline{5{\cdot}52}$.

Cloanthite....	$Ni^{2}_{1}\overline{As^{4}_{2}}$	Whitneyite..	$\overline{Cu^{45}_{36}}As^{10}_{4}$
Nickel glance.	$Ni^{4}_{2}\overline{S^{3}_{2}As^{4}_{2}}$	Zinc blende .	$Zn^{3}_{2}\overline{S^{6}_{2}}$
Copper glance	$\overline{Cu^{3}_{2}}S^{2}_{1}$	Galena	$Pb^{3}_{1}\overline{S^{3}_{1}}$
Domeykite ...	$Cu^{9}_{6}\overline{As^{4}_{2}}$.		

In both zinc-blende and galena the sulphur is present with its original volume, S^{3}_{1}, and stere, $\overline{5{\cdot}3}$, and not condensed as in the foregoing compounds.
T. C.

Inorganic Chemistry.

Peroxide of Hydrogen. By E. SCHÖNE (*Liebig's Annalen*, cxcii, 257—287).—The author attributes some of the conflicting statements which have been made regarding the properties of hydrogen peroxide to impurity of the substances used in its preparation. He fully describes the method employed by himself, in which barium peroxide prepared in the dry way is heated immediately before use to the temperature at which it begins to part with oxygen, and is then dissolved in pure nitric acid. The addition to this of solution of hydrate of barium causes the precipitation of $BaO_2.8H_2O$, which is washed by decantation and decomposed by pure sulphuric acid. The liquid poured off from the resulting barium sulphate, &c., was found to contain 1·5 grams of H_2O_2 and ·003 gram of H_2SO_4 in 100 c.c. By evaporation of this in a vacuum the author obtained a liquid containing 99·10 per cent. of peroxide of hydrogen, and of the same specific gravity as that found by Thénard for his preparation, the identity of which with the author's is thus confirmed.

The addition of a solution of hydrate of barium, strontium, or calcium to a solution of hydrogen peroxide is known to produce a precipitate of the composition $MO_2.8H_2O$. The barium compound in contact with water decomposes with evolution of oxygen gas; and the author finds that the supernatant liquid contains proportionately more barium hydrate than peroxide of hydrogen. This is explained by the combination of a portion of the peroxide of hydrogen with an equivalent quantity of barium peroxide to produce the compound BaH_2O_4. This compound the author has prepared in a pure condition by two different processes: first, by direct action on each other of the peroxides of barium and of hydrogen; secondly, by adding a determined quantity of ammonia to a solution of hydrogen peroxide containing a barium salt. In the first process the reaction is represented by $BaO_2 + H_2O_2 = BaH_2O_4$. In the second several phases may be distinguished, thus: $BaCl_2 + 2(NH_4.OH) = 2NH_4Cl + Ba(OH)_2$; $Ba(OH)_2 + H_2O_2 = 2H_2O + BaO_2$; $BaO_2 + H_2O_2 = BaH_2O_4$. The compound, BaH_2O_4, formed microscopic crystals belonging to the monoclinic system. These crystals had usually a yellow colour of more or less intensity, but by adopting certain precautions they could be obtained perfectly colourless. In this state they could not be long maintained, for the compound is very unstable, finally resolving itself in a longer or shorter time, according to the temperature, into barium peroxide, water, and ordinary oxygen gas. The paper gives ample details of the analyses of the products resulting from the decomposition of this substance under various conditions. Compounds of calcium and of strontium, analogous to BaH_2O_4, appear to exist, but the author has not yet been able to separate and examine them in a pure state.

R. R.

Note on the Ferment-theory of Nitrification. By F. H. STORER (*Am. J. of Sci.* [3], xv, 444).—In the course of some experiments on the action of certain oxidising agents on ammonium compounds, the following observations, bearing on nitrification, were made:—

Eleven bottles of 500 c.c. capacity were charged as follows: (1) with pure distilled water; (2) with solution of ammonium chloride, 0·2 mg. NH_3 per c.c.; (3) same as 2, with the addition of ferric hydrate; (4) the same, but with ferrous hydrate; (5) the same as 3, with addition of sugar-charcoal; (6) ammonium chloride, manganese dioxide, and sugar-charcoal; (7) leached peat, and pure water; (8) leached peat and ammonium chloride; (9) leached peat and ferric hydrate; (10) leached peat, ferric hydrate, and ammonium chloride; and (11) pure water.

The water used was proved in all cases to be free from nitrates and nitrites.

The "leached peat" was prepared from some bog-meadow mud, which had been thoroughly air-dried and washed with water until free from nitrates and nitrites.

Filtered and purified air was then drawn through these bottles from (11) to (1) for a fortnight, after which 100 c.c. of liquid was drawn off from each, filtered, and tested for nitrates and nitrites; these were easily detected in (8), (9), and (10), and very slightly in (7). The reaction was strongest in (10), diminishing through (9) and (8), and being weakest in (7). The strengths of (10), (9), and (8) were about as 5 : 2 : 1.

These experiments afford a striking proof of the accuracy of Millon's observation, that ammonium salts are oxidised to nitrates when in contact with humus and oxygen. On repeating the above experiment, but employing humus which had been treated with hot concentrated hydrochloric acid, no such result as the foregoing was obtained. The bottles contained much the same solutions as before, one of them having gypsum mixed with purified peat. After ten days' treatment with purified air, the only reaction for nitrates obtained was given by the contents of a bottle which had contained well-washed cotton rags, with ammonium chloride and ferric hydrate. After another week's treatment with air, the contents of the bottle containing peat mixed with gypsum gave a faint reaction for nitrates.

In a similar experiment, in which all the bottles were heated at 78° to 80°, no reaction could be obtained in any case after about 100 hours' treatment with air. The inference from these results is that the formation of nitrates and nitrites in the first experiment was due to organisms contained in the peat, which in the second and third experiments had been destroyed by the treatment with hot strong acid. Moreover, the bottles containing peat might be considered as excluded from light, since the mixture formed a thick dark-coloured mud, quite impervious to light. C. W. W.

Action of Heat on Ammonium Selenate. By C. A. Cameron and E. W. Davy (*Chem. News*, xxxviii, 133).—The ammonium selenate was prepared by saturating a dilute solution of selenic acid with ammonium carbonate and evaporating the solution to dryness, when, in spite of an excess of ammonium carbonate or ammonia, the residue possessed an acid reaction. The residue was repeatedly dissolved and evaporated with excess of the carbonate alkali, but nevertheless the residue in each case proved acid, showing that at 100°, or perhaps below, neutral ammonium selenate is partially decomposed with the formation of an acid selenate. On the temperature being raised to 180° minute quantities of ammonia gas were evolved, which increased with the rise in temperature, an acid salt forming at the same time. At 250° the decomposition proceeded further, with separation of selenium and selenium dioxide, water and nitrogen being evolved; the two stages of the decomposition may be represented by the following equations:—

$$(1)\ 4(NH_4)_2SeO_4 = 4(NH_4)HSeO_4 + 4NH_3$$
$$(2)\ 4(NH_4)_2HSeO_4 = Se + 3SeO_2 + 10H_2O + 2N_2.$$

The correctness of these equations needs confirmation by actual results. The first stage is analogous to the decomposition of ammonium sulphate by heat; in the latter case, however, there is no decomposition analogous to the second stage. L. T. O'S.

Reduction of Magnesium from its Oxide by Metallic Aluminium, and production of Artificial Spinelle. By J. H. T. Aumann (*Chem. News*, xxxviii, 108).—Mallet has shown that the oxides of barium, strontium, and calcium may be partially reduced by heating to a very high temperature with metallic aluminium, the reduced metals being volatilised; it therefore suggested itself to the author to try a like experiment with magnesium oxide. 25·46 grams of pure and freshly ignited magnesia were packed in a crucible of hard carbon, imbedding in the centre a lump of aluminium representing 8·7 grams of pure metal. The whole of the aluminium, of the magnesia, and of the crucible were, after fusion, separately treated with moderately strong, hot, hydrochloric acid, and the solutions filtered. The greyish residue left on the filters from the first two solutions was dried, ignited in a stream of oxygen to burn off some specks of carbon, and on being examined with the microscope was found to consist of minute, colourless, transparent crystals of two kinds: the one being thin elongated scales, consisting of pure alumina; the other regular octahedrons, which scratched glass readily, and on fusion with acid sodium sulphate yielded magnesia 28·99 per cent., alumina 70·81 per cent., giving the ratio, $MgO : Al_2O_3 = 725 : 689$; so that it was evident that these little crystals were artificial spinelle, $MgAl_2O_4$.

D. B.

Production of Magnesium Nitride by Smothered Combustion of Magnesium in Air. By J. W. MALLET (*Chem. News*, xxxviii, 39).—The existence of a nitride of magnesium was first noticed by Deville and Caron in connection with the purification of the metal by distillation. Briegleb and Geuther afterwards obtained this compound by passing ammonia or nitrogen over strongly heated magnesium. The amorphous greenish-yellow mass produced had approximately the composition Mg_3N_2. The author has lately observed the formation of the same substance in large quantity in the simple combustion of magnesium with limited access of air. The chief part of the metal burned is, of course, converted into oxide, with production of a temperature high enough to induce the remainder, when the supply of oxygen is limited, to unite with nitrogen.

The following three experiments show the largest absorption of nitrogen:

	Mg. used. grms.	NH_3 obtained. grms.	Equiv. Mg_3N_2. grms.	Equiv. Mg. grms.	Mg. converted into nitride per 100 pts. used.
No. 1...	2·635	0·292	0·859	0·618	23·5
No. 2...	2·204	0·286	0·841	0·606	27·5
No. 3...	3·117	0·365	0·773	0·773	24·8

D. B.

Didymium and Lanthanum. By F. FRERICHS (*Deut. Chem. Ges. Ber.*, xi, 1151).—A reply to Cleve's attack on Frerichs and Smith's paper on didymium and lanthanum. The author still maintains his former statements with regard to the fluorides, borates, and cyanides of the two elements, the accuracy of which Cleve disputes (*Ber.*, xi, 910).

T. C.

Some presumably New Earths. By B. W. GERLAND (*Chem. News*, xxxviii, 136).—The author separated from a mineral consisting of vanadate of copper and lead, found in a vein of the keuper sandstone, a group of oxides belonging to the rare earths, but possessing properties different from those already known. Their reactions are as follows:—Alkalis produce precipitates insoluble in excess of the reagent, even in presence of ammonium salts. Alkaline carbonates produce precipitates soluble in excess of the reagent: the solution is partially re-precipitated by passing carbon dioxide through it, but the precipitate is redissolved by boiling: it consists of the earth and some alkali; it fluxes at a red heat, but does not give the reactions for alumina.

The pure salts are not precipitated by barium or calcium carbonate, but are mechanically carried down in presence of iron and alumina. The oxalates are insoluble in water, acetic acid, and dilute mineral acids, but are soluble in sodium carbonate and in strong mineral acids. They form compounds with potassium sulphate, which are sparingly soluble in a concentrated solution of that salt; the more soluble portion shows the absorption spectrum of didymium more brightly than the less soluble, but neither gives the spectrum of erbium. The oxides obtained from the less soluble portion possess a leather-brown colour; those from the more soluble portion, a light-brown colour. They have no alkaline reaction, but dissolve in acids with evolution of heat. With hydrochloric, chloric, perchloric, hydriodic, periodic, and hydrofluoric acids, they form deliquescent salts soluble in water and alcohol: the sulphates, however, are less soluble, and crystallise well; they lose their water of crystallisation at 180°. L. T. O'S.

Production of Ultramarines of different Metals. By DE FORCRAND and BALLIN (*Bull. Soc. Chim.* [2], xxx, 112).—By heating blue ultramarine in sealed tubes with a concentrated solution of silver nitrate at 120° for 15 hours, a dark-yellow silver ultramarine is produced, containing 46·63 per cent. silver, exhibiting all the properties of an ultramarine, being insoluble in water and strong acids, and attacked by dilute acids with evolution of sulphuretted hydrogen and sulphurous acid. Heated with water at 100° it decomposes, forming a grey powder.

The quantity of silver which this ultramarine contains corresponds with 15·68 per cent. sodium; the original ultramarine contained about 15 per cent. sodium.

When it is heated with sodium chloride in aqueous solution in sealed tubes at 120°, or in an open flask, a maximum quantity of three-fourths of the silver is replaced by sodium; the other fourth cannot be thus replaced; in fact blue ultramarine heated with water and silver chloride takes up silver, becoming green.

By heating silver ultramarine with sodium chloride in the dry way at somewhat higher temperatures, the whole of the silver is replaced by sodium, but the ultramarine thus regenerated does not equal the original ultramarine in colour. This change is probably due to a loss of sulphur in the formation of the silver ultramarine; sulphuric acid is in fact always found in the aqueous liquid accompanying its formation.

If the whole process be repeated on an ultramarine thus regenerated, it is not possible to obtain anything but a green ultramarine, even after 50 hours' heating. If the sodium chloride in the above experiment (in the dry way) be replaced by potassium chloride, and the temperature not allowed to exceed 400°, a potassium ultramarine is obtained as a bluish-green powder. Barium-ultramarine is yellowish-brown; zinc-ultramarine is violet, and magnesium-ultramarine is grey; they may be obtained by acting on the yellow silver ultramarine with the corresponding metallic chlorides. C. W. W.

On some Compounds analogous to Chrome-iron. By J. Risler (*Bull. Soc. Chim.* [2], xxx, 110).—Gerber has prepared the chromites of calcium, barium, &c., by heating metallic chlorides with potassium dichromate. By employing potassium permanganate instead of dichromate, the corresponding manganites, $R_2Mn_5O_{11}$, may be obtained.

Calcium manganite, $CaMn_5O_{11}$, is black, crystalline, and very soluble in hot hydrochloric acid, less so in nitric acid. The *barium salt* is a dark olive-green powder containing crystalline scales, soluble in hydrochloric acid, less so in nitric acid. The *strontium salt* is a black powder, less crystalline than the calcium salt, equally soluble in hydrochloric and nitric acids. The *zinc salt* is a dark reddish-brown powder, containing a large number of crystals. The *lead salt* is a dense black powder, distinctly crystalline, not attacked by strong acids, soluble in aqua-regia. Attempts to prepare the copper salt were not successful. C. W. W.

Effect of intense Cold on Ferric Hydrate. By E. B. Shuttleworth (*Pharm. J. Trans.* [3], ix, 148).—If moist ferric hydrate be exposed to a temperature of −23·5°, it is changed to a blackish-brown powder, which has lost the property of dissolving in citric acid. When heated, it loses 27·2 per cent. of its weight, and therefore appears to be a hydrated oxide, intermediate between hydrated ferric oxide and certain varieties of brown iron ore.

When a solution of dialysed iron is subjected to cold sufficient to produce complete congelation, the frozen mass on thawing deposits the iron oxide in reddish-brown scales. E. W. P.

Ammonio-argentic Iodide. By M. Carey Lea (*Amer. Jour. Sci.* [3], xv, 379).—Silver iodide absorbs 3·6 per cent. of its weight of ammonia gas, forming a compound $2AgI.NH_3$.

The well-known white compound of ammonia with silver iodide rapidly loses its ammonia by washing with water, or on exposure to the air. When exposed to light under ammonia, it first darkens and then bleaches again, the more rapidly as the ammonia can escape more easily, and not at all when the ammonia cannot escape. The ammonia at the same time takes up iodine in small quantity. When darkened silver iodide is left under ammonia in the dark for a day or two, it assumes a pink colour.

Ammonio-argentic iodide thus passes, under the influence of light, from white to violet and then to black; the black substance becomes brown when washed with water; and the brown substance, exposed under ammonia, becomes yellow in the light, and pink in the dark.

C. W. W.

On Silver Arsenite insoluble in Aqueous Ammonia. By J. R. Santos (*Chem. News*, xxxviii, 94).—In the text-books, it is usually stated that the light-yellow precipitate of silver arsenite is soluble in excess of ammonia. Having noticed that the yellow precipitate obtained by mixing solutions of silver nitrate and sodium arsenite, if washed several times by decantation, did not dissolve (at any rate completely) in aqueous ammonia, but assumed a well-marked crystalline character and a darker yellow colour, the author investigated this subject more fully, his results being as follows:—The normal tribasic arsenite of silver is not, as such, soluble in ammonia, but becomes readily soluble in presence of alkaline nitrates; it is slowly and imperfectly decomposed by the continued action of ammonia, forming perhaps a silver ammonium salt. A silver arsenite containing in combination or admixture a larger proportion of arsenic than that of the tribasic salt is at once soluble in ammonia by itself, a corresponding difference of solubility in acetic acid being, under these conditions, observable in each case. D. B.

Specific Gravity of the Vapours of the Chlorides of Lead and Thallium. By H. E. Roscoe (*Deut. Chem. Ges. Ber.*, xi, 1196—1197).—The substance, the vapour-density of which was required, was placed in a glazed porcelain globe with a long neck and of known volume, and exposed to a bright red heat in a muffle furnace. The temperature of the globe was determined by the method of specific heat, a large piece of platinum being employed for the purpose, and the result checked by the simultaneous determination of the vapour-density of mercury under the same conditions. The globe was loosely closed with an earthenware stopper and allowed to remain in the furnace until the evolution of vapour ceased, when it was quickly removed and the temperature determined as described. The residue remaining in the globe was afterwards estimated by the ordinary methods. In this manner the following results were obtained for thallium chloride and lead chloride:—

Thallium chloride.		Lead chloride.	
Temperature.	Spec. grav. of vapour (air = 1).	Temperature.	Spec. grav. of vapour (air = 1).
859°	8·15	1046°	9·12
828	8·28	1089	9·72
1015	8·06	1077	9·51
849	7·43	1070	9·64
1026	8·75		
852	8·60		
837	7·84		
Calculated for $TlCl$ = 8·49		Calculated for $PbCl_2$ = 9·62.	

These results prove that the molecular weights of the chlorides of lead and thallium in the state of vapour are 277 and 238 respectively, and the corresponding formulæ $PbCl_2$ and $TlCl$. T. C.

Alloys of Gold and Mercury. By M. Kasantseff (*Bull. Soc. Chim.* [2], xxx, 20).—The liquid amalgams obtained by squeezing alloys of gold and mercury through chamois-leather always contain (at the ordinary temperature) 0·126 per cent. of gold. At 0° the proportion is ·110 per cent. gold; at 20°, ·126 per cent.; and at 100°, ·650 per cent.; these amalgams, therefore, behave like aqueous solutions. When glass capillary tubes are used instead of chamois-leather for the separation of the liquid amalgam, no relation can be discovered between the diameter of the tube and the percentage of gold.

The residual alloys left after the action of nitric acid on solid or liquid gold-amalgams are not homogeneous, which proves that there probably exist definite compounds of gold and mercury dissolved in excess of mercury, just as in aqueous solutions definite hydrates are mixed with excess of water. C. W. W.

Artificial Crystals of Gold, and Gold-amalgam. By A. H. Chester (*Amer. Jour. Sci.* [3], xvi, 29).—Well-defined octohedral faces may occasionally be observed on bars of very pure gold, sometimes slightly raised above the general surface and attaining half an inch in length. Gold precipitated by the battery (for dental purposes) assumes the form of fern-leaves, the angles of the branches of which are constant on one side of the same leaf, but vary very much in different specimens and on the two sides of the same specimen. The smallest angle observed was 30° 36′, and the highest 80° 30′; the greatest angle formed between the two sets of branches was 122° 36′. These crystals do not show distinct faces even under a magnifying power of 300 diameters.

When a film of amalgam is formed on the surface of pure gold, and the mercury then driven off by a gentle heat, crystals may be occasionally observed; if nitric acid be used to dissolve the mercury, distinct crystals may easily be obtained. They are hexagonal prisms, the angle being 119° 53′; they sometimes consist of only the basal termination, and are occasionally hollow. C. W. W.

Weldon's Process for the Recovery of Manganese. (*Dingl. polyt. J.*, ccxxix, 51—54).—This paper does not give any important improvements in the Weldon process; however, a description of this method is given which is well arranged, and therefore worthy of notice. Lamy (*Bull. Soc. d'Enc.*, 1877 [iv], 428) states that in the preparation of chlorine from manganese dioxide and hydrochloric acid at a temperature lower than 100°, one-half of the chlorine present in the acid remains in the decomposing vessels in the form of manganous chloride. This residue contains, besides the manganese used, from 8 to 15 per cent. of undecomposed hydrochloric acid, a considerable quantity of iron, and other admixtures present in manganese dioxide.

Weldon's process depends on the fact, that manganous oxide is converted into manganese peroxide by the double action of an excess of lime and a stream of air at 55°. By exposing manganous oxide to air alone, the latter is only converted into manganic oxide. This change may be explained also by assuming that one-half of the protoxide is converted into the peroxide, forming a salt with the former, in which the peroxide plays the part of an acid ($Mn_2O_3 = MnO.MnO_2$). However, by oxidising manganous oxide in presence of a corresponding quantity of lime, partly in suspension, partly dissolved in calcium chloride, a complete formation of peroxide is obtained, a compound of the formula, $CaO.MnO_2$, being formed. For the preparation of chlorine, it would be of no consequence to produce either $MnO.MnO_2$ or

$CaO.MnO_2$, both compounds requiring the same quantity of hydrochloric acid. However, by the formation of the latter compound, much time is saved, $CaO.MnO_2$ requiring only one-tenth of that needed by the former. In the reaction, this calcium manganite forms an intermediate body, which is converted into calcium dimanganite ($H_2O.CaO + 2MnO_2$); the latter, with the same quantity of hydrochloric acid, gives more chlorine. By treating calcium manganite with manganous chloride, according to the equation:

$$\text{I. } 2(CaOMnO_2) + MnCl_2 + H_2O = H_2OCaO2MnO_2 + CaCl_2 + MnO,$$

one-half of its contents of lime only is used for the formation of calcium chloride. On this fact depends the formation of the bimanganite in the process. By introducing air into the mixture (I), the other half of the protoxide is converted into the peroxide. According to the equation $MnCl_2 + 2CaO + O = CaCl_2 + CaOMnO_2$, 1 equivalent of manganous oxide requires 1 equivalent of lime, in which case the recovery of manganese is complete. Since crystalline compounds are formed in the apparatus by the application of the above proportions, which render the working impracticable, and often convert the mixture into a solid mass, Weldon reduced the quantity of lime to 0·6 equivalent. Although the recovered product showed a smaller yield (79 per cent.), this was compensated by the smaller quantity of hydrochloric acid required for saturating the bases.

By starting with a mixture consisting of manganese peroxide and manganous oxide, calcium chloride, and water, we obtain the following reactions:—$100MnCl + 160CaO$ are brought into the oxidising apparatus, besides water and more or less calcium chloride. These give: $100MnO + 60CaO + 100CaCl$. By passing air into this mixture, we have $100MnO + 60CaO + 86O = 86MnO_2 + 14MnO + 60CaO$ (according to analysis). The second part of the equation may be written thus:—

$$\text{II. } 48(CaO.MnO_2) + 14(MnO.MnO_2) + 12(CaO.2MnO_2), \text{ or}$$
$$\text{III. } 86MnO_2 + 60CaO + 14MnO.$$

By adding $24MnCl_2$ (residual lyes), we obtain from $48(CaO.MnO_2) + 24MnCl. = 24(CaO.2MnO_2) + 24MnO + 24CaCl_2$. By introducing air and absorbing $12O$, we obtain from $24MnO$ yet $12(MnO.MnO_2)$, and the mixture (II) gives:—

$$36(CaO_2 2MnO_2) + 26(MnO.MnO_2) + 24CaCl_2, \text{ or}$$
$$\text{IV. } 98MnO_2 + 36CaO + 26MnO + 24CaCl_2.$$

From IV it is seen that 124 manganous oxide give 98 peroxide, *i.e.*, 79 per cent.; together 60CaO and MnO, or 50 per cent.

Before the addition of the residual lyes, we had, according to equation (II), 86 per cent. of peroxide, the decrease taken place being therefore 7 per cent.; and the quantity of lime and manganous oxide together amounted to 74 per cent., showing a decrease of 24 per cent.

The loss in working amounts to 5 per cent. of manganese on the total quantity present, which is due to the fact that sulphuric acid is present in commercial hydrochloric acid. This loss may be reduced to 2·5 per cent. by washing the gypsum precipitate in filter presses.

D. B.

Mineralogical Chemistry.

The Chemical Character of Silaonite from Guanajuato, Mexico. By H. D. BRUNSO (*Chem. News*, xxxviii, 109).—V. Fernandez and S. Navia described in *La Republica*, 1873, as a new species a selenide of bismuth found with guanajuatite in the mine of Santa Catarina, and on the basis of an incomplete analysis of confessedly impure material attributed to it the formula Bi_3Se. The improbability of this formula suggests itself at once, since it assumes the presence of an odd number of perissad atoms. An authentic specimen of the so-called silaonite having been procured, the author examined it with a view to ascertain whether it contains any free metallic bismuth in admixture or not. Analysis showed that bismuth was present in a free state, which seems therefore sufficient reason to believe that this species is but a mixture, and not a distinct mineral. The surplus bismuth is chiefly present as native metal, but also as carbonate and hydrate. D. B.

Action of Iodine, &c., on Natural Sulphides. By H. C. BOLTON (*Chem. News*, xxxviii, 168—170).—The author has studied the action of iodine on the following minerals, when finely powdered, and in presence of water. They were mixed together and allowed to stand for some hours in the cold, the action noted, the mixture boiled, and the action again recorded. The following are the results:—

Stibnite, strongly attacked; the solution, which has a brown colour, contains sulphuric acid and antimony.

Molybdenite not attacked, even when boiled.

Argentite, in the cold, yields a red solution and yellowish-white precipitate; excess of iodine completely decomposes the mineral.

Galenite is decomposed in the cold with the formation of lead iodide; heat increases the action.

Bornite in the cold yields a brown-red solution; cuprous iodide formed; decomposition increased by heat.

Sphalerite: crystalline precipitate and dark-red solution in the cold; heat completes the decomposition.

Chalcocite is strongly attacked with excess of iodine; red solution formed; heat increases the action; very little cuprous iodide formed.

Cinnabar is attacked in the cold; iodide of mercury formed on heating.

Pyrrhotite is attacked in the cold; solution becomes dark on heating.

Pyrite is only incompletely decomposed even on heating. H. Wurtz (*Am. J. Sci.* [2], xxvi, 190) states that pyrite is not decomposed by iodine solution, only a small quantity of iron separating out.

Niccolite is strongly attacked in the cold, forming a green solution, which changes to brown on heating with excess of iodine.

Smaltite is attacked in the cold; heat increases the action and produces a red solution.

Chalcopyrite: deep-red solution in the cold; action increased by heat; no precipitate formed.

Tetrahedrite, *ullmanitite*, and *arsenopyrite* behave like chalcopyrite.

Bournonite gives a deep-red solution in the cold. On heating, a precipitate of lead and cuprous iodide is formed.

Beside the above sulphides, the action of iodine on the following minerals was studied:—

Limonite, *hœmatite*, *magnetite*, the *manganese oxides*, *pyromorphite*, and *calamine* are not attacked even on boiling. *Cuprite* is decomposed in the cold, forming a bright-green precipitate of $CuIO_5$(?). *Brucite*, *calcite*, and *natrolite* are decomposed on heating. *Anglesite*, *cerussite*, and *vivianite* are feebly attacked in the cold, but strongly on heating.

The author has also studied the action of potassium iodide and citric acid on the following natural sulphides and other minerals.

Stibnite, *argentite*, *sphalerite*, *chalcocite*, *bornite*, and *ullmannite* are decomposed in the cold, with liberation of sulphuretted hydrogen; heat increases the action. In the case of galena, lead iodide is formed in yellow crystalline plates, sulphuretted hydrogen being evolved. A similar action occurs with *cinnabar*, mercuric iodide being formed.

Arsenopyrite is decomposed in the cold without evolution of sulphuretted hydrogen; heat increases the action.

Pyrrhotite, *chalcopyrite*, and *bournonite* evolve sulphuretted hydrogen only on heating.

Pyrite, *niccolite*, and *smaltite* are strongly attacked when boiled, but evolve no sulphuretted hydrogen.

Tetrahedrite is slightly attacked in the cold; the action is increased by heat.

Molybenite is not acted on.

Similar results were obtained by substituting tartaric or oxalic acid for citric acid. Cinnabar, when treated with oxalic acid and potassium iodide, is rapidly decomposed in the cold, and also on heating, when the solution cools, acid potassium oxalate, and mercuric iodide crystallise out. The reaction is probably expressed as follows:—

$$2H_2C_2O_4 + HgS + 2KI = 2KHC_2O_4 + HgI_2 + H_2S.$$

Magnetite is acted on by a mixture of potassium iodide and citric acid.

Franklinite and *hœmatite* are feebly attacked in the cold; more strongly on heating. *Chromite* not attacked.

The oxides of manganese yield deep-brown solutions.

Anglesite and *pyromorphite* are decomposed in the cold, with formation of lead iodide.

Cuprite in the cold gives a yellowish-white precipitate and a colourless solution; the latter is blue, if heat is applied at the beginning.

The action of citric acid and potassium bromide on the minerals was also studied. The bromide, however, not being decomposed so readily as the iodide, gave no characteristic reactions. Those minerals which yield to the action of the iodide only on heating resist that of the bromide altogether. L. T. O'S.

Friseite, a Mineral resembling Sternbergite. By C. Vrba (*Jahrb. f. Min.*, 1878, 531).—This mineral occurs in the Joachimsthal on compact liver-pyrites, accompanied by pseudomorphs of argentiferous pyrites and dolomite. The crystals are orthorhombic. Observed faces: $0P$, $\infty\bar{P}\infty$, $3\bar{P}\infty$, $\frac{1}{2}\bar{P}\infty$. They are always in the form of thick tablets, the basal face predominating. Twins occur, as in sternbergite, according to ∞P. Cleavage basal, very distinct. Hardness = 2. Sp. gr. = 4·217—4·220. Colour dark pinchbeck-brown. Before the blowpipe, the mineral behaves like sternbergite. Chemical composition, according to K. Preis, 37·59 per cent. S, 29·25 Ag, 33·16 Fe = 100. Hence the formula, $Ag_6Fe_{13}S_{26}$.

H. W.

Baryto-calcite from Långban. By A. Sjögren (*Jahrb. f. Min.*, 1878, 527).—This mineral occurs in spathose and granular masses, sometimes also in distinct crystals ($\frac{1}{4}$—1 centimeter in size), accompanied by hausmannite and hedyphanite. In a thin section, the baryto-calcite appeared tolerably pure, containing only small quantities of hedyphanite and scheelite. Sp. gr. = 3·46 (Lundström). Two analyses by C. H. Lundström gave:—

	BaO.	CaO.	MgO.	FeO.	MnO.	CO_2.
Spathic....	50·89	17·64	0·40	0·42	0·24	29·32
Granular ..	44·13	18·19	2·51	0·18	1·12	30·40

	Insoluble.	PbO.	As_2O_5.	
Spathic	0·70	0·37	—	= 99·98
Granular....	2·00*	1·39	trace	= 99·92

H. W.

Occurrence of Berzeliite and Karyinite. By A. Sjögren (*Jahrb. f. Min.*, 1878, 327).—The author examined thin sections of these two minerals from the dolomitic limestones near Långban. The berzeliite is white and isotropic, whereas the karyinite—so called from its light nut-brown colour—appears light yellow and anisotropic. In six thin sections examined, the karyinite was surrounded by a band of berzeliite more or less broad; so that, according to Sjögren, berzeliite is to be regarded as an altered karyinite, the lead and manganese having been removed, while the arsenates of calcium and magnesium have remained.

H. W.

Cerussite from Rodna in Transylvania. By C. Vrba (*Jahrb. f. Min.*, 1878, 532).—The cerussite of Rodna has hitherto been known only in small milk-white prisms. Vrba has observed the following forms: ∞P, $\infty\breve{P}\infty$, $\infty\bar{P}\infty$, $\frac{1}{2}\breve{P}\infty$, $\breve{P}\infty$, $2\breve{P}\infty$, $\infty\breve{P}3$, P. The crystals, which have a strong lustre, are always formed in twins or drillings, according to ∞P. The twin-formation is several times repeated, so that smaller crystals are often implanted on the principal individuals. The crystals are mostly prismatically elongated in the horizontal direction, less frequently tabular, parallel to the brachypinacoïd. The dome-faces are always striated parallel to their combination-edges. The prismatic and pyramidal faces are always smooth and shining. A peculiarity of the Rodna cerussites consists in their unmistakeable hemimorphous development, the faces of the brachypinacoïd and those of $\frac{1}{2}\breve{P}\infty$ being greatly developed on one side and narrow on the other. The faces $\breve{P}\infty$ and $2\breve{P}\infty$ occur for the most part only on the side which is distinguished by the greater development of the brachypinacoïd. H. W.

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* Chiefly barium sulphate.

Efflorescence of Glauber Salt at Klausenburg. By A. Koch (*Jahrb. f. Min.*, 1878, 529).—On various places, mostly on bare declivities and in hollows, even on the banks and on the boulders of the Kajanta Bach in Transylvania, there occurs a white saline efflorescence, which, on recrystallisation, yields beautiful many-faced crystals exhibiting the known forms of Glauber salt. Chemical analysis also showed that it is an impure sodium sulphate. The quantity in which it occurs is remarkable. The materials for its formation are furnished by the underlying rock, which is a saliferous clay identical with that of the Transylvanian salt-beds, and by the finely-divided iron pyrites diffused through it. H. W.

On a Glassy Mineral which forms on the Rocks of the Mediterranean Coasts. By S. Cloez (*Jahrb. f. Min.*, 1878, 530).—At the meeting of the Geological Society of Nizza, there were exhibited fine specimens of a dolomitic limestone, covered more or less thickly with a black varnish-like coating, exhibiting batryoïdal forms. This substance, found chiefly in the neighbourhood of Cape Ferrat, gave by analysis:—

$CaCO_3$.	$MgCO_3$.	F_2O_3.	SiO_2.	NaCl.	Organic matter.	Water.	
0·9180	0·0090	0·0025	0·0122	0·0049	0·0071	0·0456	= 0·9993.

It is doubtless produced by the action of the sea-waves on the limestone rocks of the locality. H. W.

Adamine Crystals from Laurium. By H. Laspeyres (*Jahrb. f. Min.*, 1878, 532).—The crystals of adamine occur in two types, the first exhibiting chiefly the faces ∞P, $\bar{P}\infty$, $\infty\breve{P}2$, and $\infty\breve{P}\infty$; these crystals are striated parallel to the macrodiagonal, and colourless. The crystals of the second type are more prismatic, and have a somewhat larger number of faces, the principal forms being ∞P, $\infty\bar{P}2$, $\infty\bar{P}\infty$, $\breve{P}\infty$, and $0P$. They have a fine emerald-green colour, arising from a not inconsiderable amount of copper. The principal angles, determined by measurement and calculation, are $\infty P = 90° 14' 18''$; $\bar{P}\infty = 108° 26' 56''$; $\breve{P}\infty = 71° 19' 22''$.

The two types of adamine from Laurium cannot be referred crystallographically one to the other. Whether this diversity arises from a difference of chemical constitution is a point which remains to be investigated; the same remark applies also to the difference between the angles of the Laurium crystals and those of Chanarcillo, which were measured by Des Cloizeaux. H. W.

Composition of Aeschynite and Samarskite. By C. RAMMELSBERG (*Jahrb. f. Min.*, 1878, 529).—1. Aeschynite, sp. gr. 5·16, gave by analysis:—

Nb_2O_5.	TiO_2.	ThO_2.	Ce_2O_3,La_2O_3,Di_2O_3.	Y_2O_3,Er_2O_3.	Fe_2O_3.	CaO.
32·51	21·20	17·55	19·41	3·10	3·71	2·50=99·98

Hence the formula $R_2Nb_2(Ti,Th)_3O_{14}$, or else $R_3Nb_3(Ti,Th)_4O_{20}$.

2. Samarskite, (*a*.) from Miask, sp. gr. = 5·672; (*b*.) from Mitchell County, North Carolina, sp. gr. = 5·839. In neither case could Rammelsberg detect the presence of acids of zirconium or thorium, which, according to some authorities, exist in this mineral:—

	SnO_2.	TiO_2.	SiO_2.	Ta_2O_5.	Nb_2O_5.	Y_2O_3.	Er_2O_3.
a.	0·22	1·08	—	—	55·34	8·80	3·82

Ce_2O_3(Di).	Fe_2O_3(Mn).	UO_3.
4·33	14·30	11·94 = 99·83.

SnO_2.	TiO_2.	SiO_2.	Ta_2O_5.	Nb_2O_5.	Y_2O_3.	Er_2O_3.
0·16	—	0·56	14·36	41·07	6·10	10·80

Ce_2O_3(Di).	Fe_2O_3(Mn).	UO_3.
2·37	14·61	10·90 = 100·93.

The mineral therefore consists essentially of a heminiobate (tantalate) isomorphously mixed with a uranate; and as U : (Nb,Ta) = 1 : 10 nearly, the formula of samarskite is $\left.\begin{matrix}8R_4Nb_8O_{21}\\ R_4U_5O_{21}\end{matrix}\right\}$, or,

$$8(2R_2O_3.3Nb_2O_5) + 2R_2O_3.5UO_3\ [R = Y, Er, Ce(Di), Fe(Mn)].$$

H. W.

Rutile from Modriach. By V. HANSEL (*Jahrb. f. Min.*, 1878, 528).—In the gneiss near Madriach, to the west of Sigis in Styria, especially in the quartz-masses of the gneiss, rutile occurs embedded in separate crystals, remarkable both for their size and for their development. They are from 1 c.m. long and 1½ thick to 2½ c.m. long and 2 c.m. thick. Most of them are fully developed at both ends, and the faces are often coated with mica. Most of the crystals exhibit the faces ∞P, $\infty P\infty$, P, and $P\infty$, sometimes also $P3$, $\infty P\frac{3}{2}$ and $\infty P3$. The ∞P-faces usually exhibit vertical striation. Sometimes the crystals acquire a thick tabular habit by predominance of two parallel prismatic faces, or a monoclinic habit by predominance of the pyramidal faces.

Hansel mentions, also, another locality of rutile, viz., Bruck an der Mur in Styria, where there has been found a large crystal 3½ c.m. long and 3 c.m. thick, exhibiting the combination $\infty P . \infty P\infty . P . P\infty$. Like the rutiles of Modriach, it is coated with thin layers of mica, and hence has a yellowish tinge.

H. W.

Quartz-crystals from Kremnitzka.—Crystallographic Observations on the Copper of Lake Superior.—Unusual and Anomalous Faces on Garnet from the Pfitschthal in Tyrol. By G. VOM RATH (*Jahrb. f. Min.*, 1878, 528, 530, 531).

Optical Character of Tridymite from the Euganean Hills. By M. SCHUSTER (*Jahrb. f. Min.*, 1878, 533).—The tridymites examined are found on Monte Gioino, near Teolo, and near Zovon, in cavities of an oligoclase trachyte. They are small crystals of the known forms, mostly united in twins, drillings, and tetralings. Optical examination—which must be made on extremely thin plates—showed that tridymites viewed in polarised light appear as combinations of a number of individuals arranged as twins. One of the prepared plates, examined in a Nörremberg's polarising microscope, showed very distinctly the first coloured ring of an axial system, whence it may be inferred that tridymite belongs either to the monoclinic or to the triclinic system. Moreover, the optical principal sections of tridymite are not parallel to either of the external faces. For the two principal sections visible at the end-face, this result follows from the measurements; but the third principal section is also inclined to the same edge, and on one of the very narrow prism-faces the angle between principal section and edge was found to be about 10°. From these observations it follows that tridymite belongs to the triclinic system, and that it is only in consequence of the oft-repeated twin-formation that forms are produced which, in their outlines, as well as in their angles, approximate closely to those of the hexagonal system. The tridymites of Pachuca and of Gereczes, in Transylvania, exhibit in polarised light appearances which lead to the inference that they are similar in structure to those of the Euganean Hills. H. W.

Analysis of Tabasheer from Sumatra. By J. H. S. AUMANN (*Chem. News*, xxxviii, 108).—A specimen of tabasheer from Palembang, in Sumatra, presented the appearance of irregularly shaped fragments, from the size of a pea to that of half a walnut, generally bluish-white in colour, some bits dark, smoke-grey, or brownish; easily broken between the fingers; finely porous, and strongly adherent to the tongue. Sp. gr. in mass, including air in the pores, equals about 0·5; after pulverisation and boiling in water to expel air, it equals 1·96. Some of the whitest pieces picked out yielded on analysis:—

SiO_2.	Fe_2O_3.	CaO.	Na_2O.	K_2O.	NH_3.
94·196	0·098	0·125	0·596	0·016	distinct traces

Org. matter.	H_2O.	
0·221	4·057	= 99·309 p. c.

This analysis, compared with that by Rost van Tonningen of tabasheer from Java, represents less water and greater freedom from any other constituents than silica and water. The difference as regards the quantity of alkaline metals present is very marked. He found:—

SiO_2.	Fe_2O_3.	CaO.	K_2O.	Org. matter.	H_2O.	
86·387	0·424	0·244	4·806	0·507	7·632	= 100·00 p.c.

D. B.

The Apophyllite of the Radauthal. By O. LÜDECKE (*Jahrb. f. Min.*, 1878, 527).—The gabbro of the Radauthal in the Hartz is intersected by veins of quartz, in the cavities of which, partly on quartz-crystals, partly on cockscomb-shaped aggregates of prehnite, are implanted small crystals of apophyllite, exhibiting the combination P. ∞P∞, also often with 0P and a ditetragonal prism. The diameter of these crystals is 0·5—1 mm., in the direction of the principal axis, and 0·3—0·5 mm. in the direction of the secondary axis. They are mostly white, and have a rough surface. Out of about 100 specimens only 10 could be selected which seemed likely to yield exact measurements. These gave:—Axial ratio $a : c = 1·12138$; angle of the terminal edges of $P = 104° 41'$; of the lateral edges $= 119° 33'$; $0P : P = 120° 13'$. It is well known that apophyllite crystals from different localities exhibit variations in the magnitude of their angles; such variations, moreover, occur in crystals from one and the same locality. According to Lüdebeck, the pyramidal angles in five crystals from the Radauthal differed among themselves by a quarter of a degree.

H. W.

Analysis of Precious Garnet from the Cape of Good Hope. By C. Knap, Jun. (*Chem. News*, xxxviii, 109).—These fragments presented themselves of fine deep-red colour, clear, and for the most part free from flaws; of an average size, not exceeding about 0·2 or 0·3 gram in weight; irregular in shape, sometimes exhibiting water-worn, rounded surfaces; very rarely any distinguishable crystal faces; for the most part splintery and conchoïdal surfaces of fracture. Sp. gr. 3·86. Analysis gave:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.
39·06	21·02	2·69	18·70	0·58	12·09	5·02 = 99·16 p. c.

This gives the ratio $M''O : R_2'''O_3 : SiO_2 = 660 : 221 : 651$, and the usual orthosilicate formula $M_3''R_2'''Si_3O_{12}$.

D. B.

On Lettsomite, and the Hypersthene and Labradorite of the Hyperite of Aveyron. By F. Pisani (*Compt. rend.*, lxxxvi, 1418—1420).—*Lettsomite.*—This mineral was found as a thin covering of radiating capillary crystals upon the surface of other minerals in the Garonne mine of the Department of Var. Analysis gave numbers closely agreeing with those obtained by Percy from the lettsomite of Bannat. The author considers that lettsomite should rank as a distinct mineral species, on account of its fibrous structure, and the close resemblance in composition shown by samples collected from widely separated localities. Other minerals analysed by the author, which more or less resembled woodwardite, and also the luysite described by Collins, are considered to be mixtures undeserving the names of separate species.

Hypersthene.—This was contained in large quantity in hyperite from a nonspecified French locality; the author undertook a complete analysis because hypersthene is not a mineral of common occurrence in Europe, and in France has been found only in small crystals in the Capucin Rock on Mont Dore. A fragment from Arvien in Aveyron yielded the same density as the sample examined by the author, and was undoubtedly the same substance. The author gives the details of the crystallographic and analytical examination of this hypersthene; it was somewhat less rich in iron than a Norwegian sample analysed by him some years since. The results yielded by an analysis of the labradorite which accompanied the hypersthene are also given by the author. F. C.

Examination of the Products of Weathering of Allanite. By J. R. SANTOS (*Chem. News*, xxxviii, 95).—The allanite found in large quantity in Amherst Co., Virginia, occurs for the most part in detached lumps, from a few ounces to three or four pounds in weight, showing rough crystalline faces as well as fractured surfaces, and often coated with a crust (the result of weathering), varying from a mere film to a fifth of an inch in thickness. It seemed a matter of interest to examine this crust, in order to see how the mineral in question changes chemically, whilst disintegrating by partial exposure to atmospheric influence in contact with decomposing felspathic rocks. The crust where thickest was found to be composed of two layers, an outer one nearly white, and an inner one of brick-red colour; both were earthy and pulverulent in texture. The following analyses were obtained:—

	Crust.		Original mineral.
	Outer layer.	Inner layer.	
Silica	21·37	8·05	31·23
Alumina	20·66	16·83	16·45
Ferric oxide	12·24	37·14	3·49
Ferrous oxide	—	—	13·67
Cerous „	21·90*	7·13*	11·24
Lanthanum oxide	—	—	9·90
Didymium „	—	—	
Yttria	—	—	1·65
Glucina	1·95	0·94	0·24
Lime	—	—	8·69
Magnesia	—	—	0·22
Water	21·37	29·55	2·28
	99·49	99·64	99·06

Hence it appears that calcium, magnesium, yttrium, and didymium have been entirely removed, the last-named so completely that no absorption-bands could be seen with the spectroscope in a strong solution contained in a cell 6 inches through; lanthanum has almost disappeared; the quantity of cerium has been somewhat reduced, and then relatively much increased by removal of other substances; iron has been first peroxidised, and its relative amount largely increased by removal of other constituents, and has subsequently been itself in great part removed; alumina and glucina have resisted removal, and have therefore relatively accumulated; much silica has been withdrawn, but the more rapid removal of iron in the outer layer has again led to an apparent increase; and water has largely increased by formation of ferric hydrate, diminishing again as this latter has been removed in the outer layer. D. B.

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* Including a trace only of lanthanum oxide, obtainable by treatment with yellow mercuric oxide and potassium permanganate.

The Felspar Pseudomorphs of the Wilhelmsleite, near Ilmenau. By C. Dalmer (*Jahrb. f. Min.*, 1878, 225—264).—The felspar pseudomorphs of this district are characterised by the fine development of the crystals, and by a smaller amount of alumina than other felspar pseudomorphs. They have previously been described (*Pogg. Ann.*, xlix, 381), (*Pseudomorphosen des Mineralreichs*, III *Nachtrag*, 201, Blum), (*Lehrb. d. Chem. Geologie*, 2nd edition, ii, 428, G. Bischoff), (*Zeitsch. d. Deutschen Geol. Ges.*, 1876, 22, Laufer), but mostly macroscopically; the author therefore undertook a geognostic, chemical, macroscopical, and microscopical investigation of them, with the results given briefly as follows :—

Geognostic Description of the Rock:—The crystals which are the subject of this paper are found enclosed in a vein of quartz-porphyry, which penetrates the granite on the southern declivity of the Wilhelmsleite, near Ilmenau, lying between Manebach and Stützerbach. The crystals are found in large quantities amongst the rubbish of numerous old mines. The vein-rock varies considerably in character, as much in the number and size of the enclosures as in their colour, quartz and orthoclase crystals sometimes occurring in enormous quantities and of great size, at other times only a quartz grain here and there, with large isolated felspar crystals, and occasionally an entire absence of enclosures. All these varieties occur very near to one another, so that they appear to have been formed simultaneously. The porphyry occurs in two types, the first consisting of a light lilac-coloured ground-mass, penetrated by small dark-brown laminæ, a great quantity of large quartz crystals exhibiting the complete pyramid, sometimes 7 mm. in size, and more or less decomposed felspar crystals, which attain occasionally a size of 2 to 3 cm. The second type is cherry-red in colour, rough to the touch, and contains here and there quartz grains and large felspar crystals. No nests of kaolin were found in this rock, but some very fine branching clefts were observed (in some sections) filled with silica. A microscopical examination of the rock showed the ground-mass to be clouded and translucent, but this translucency was obscured by numerous enclosed "ferrite-grains." The quartz sometimes exhibited crystalline outlines, but generally consisted of irregular grains containing the usual enclosures. The felspar crystals were much decomposed.

Macroscopical Description of the Pseudomorphs.—The crystals are of two types, those of the first being tabular, through the clinopinacoïd, and mostly twins according to the Carlsbad law, those of the second type being rectangular, prismatic, and always single. Sometimes irregular intergrowths of two or more crystals occur, which are occasionally of the same type, and occasionally crystals of both types are intergrown, but there is no regularity in the growths, as the clinodiagonal axes of the two individuals do not intersect at a constant angle, but at varying angles, having occasionally even a parallel position. On breaking one of these crystals, it is at once evident that they are not of homogeneous composition, but consist of—(1) grey shimmering laminæ of calcium carbonate; (2) yellowish-brown iron ochre; (3) a white, non-cleavable, lustreless mass, apparently silica; (4) a light-green substance, which is soft enough to be scratched by the finger-nail.

Microscopical Description.—Sections of the pseudomorphs made parallel to the clino-diagonal principal section were examined, and they exhibited the following features. A yellowish-brown network of iron-ochre penetrates the mass, the meshes being sometimes narrow and sometimes broad, often enclosing calcite, in which again is enclosed a dark iron compound, very probably formed simultaneously with the calcite. The yellow iron-ochre, on the other hand, appears to have been a later formation, and in some instances displaces the calcite substance. The felspathic substance of the original crystal is also much altered, the results of the decomposition being—(1) colourless, porous silica, which exhibits occasionally intense and variegated colours; (2) a light-green, clouded, weakly shimmering substance; (3) small green cubical or octohedral crystals. The separated silica penetrates the threads of the meshes already alluded to, sometimes completely displacing the iron-ochre; it is never free from enclosures, and is always penetrated by numerous dark grains of ferrite. In conjunction with the silica, the light-green substance (No. 2) occurs in large round bottle-shaped masses and irregular angular grains, which sometimes enclose particles of silica. The small greenish crystals observed occur always in the amorphous green substance; their size oscillates between ·01 to ·02 mm., and on this account it was found quite impossible to determine their optical and other properties, more especially as thin sections of them were always accompanied by a film of the amorphous green substance. Colourless microlites were also observed. In one preparation the author observed a predominating whitish mass, which appeared to be filled with an extremely fine light-grey dust, enclosing specks here and there of separated silica.

Chemical Examination.—The author submitted the pseudomorphs to a careful quantitative analysis, having first obtained an average sample by taking a number of crystals in an equal state of decomposition, and pulverising them. A weighed portion was treated with acetic acid, which dissolved out the calcium carbonate, the amount of which was ascertained. The insoluble residue from the acetic acid treatment was dried in a water-bath and weighed, then divided into three portions, and treated as follows:—

(1.) A portion was boiled in hydrochloric acid, the resulting solution evaporated down to dryness, and the constituents determined (Fe_2O_3, Al_2O_3, Mn_2O_3, MgO, K_2O). The residue insoluble in the hydrochloric acid was then well boiled with a solution of sodium carbonate, and the amount of soluble silica determined. The insoluble residue remaining after the last-mentioned treatment was then well washed, dried, and treated with hydrofluoric acid, and its constituents determined (Fe_2O_3, Al_2O_3, K_2O, MgO, SiO_2).

(2.) A portion was sealed up in a glass tube with sulphuric acid, and heated up to 160°, the resulting solution made up to 100 c.c., and a portion taken for titration for ferrous oxide. The residue insoluble in sulphuric acid was boiled in sodium carbonate solution, and the amount of soluble silica determined, the residue from this being then fused with sodium carbonate, and the constituents determined.

(3.) A portion was ignited, and the loss in weight determined; the residue was then fused with sodium carbonate and analysed as usual.

As the result of the above processes, it was found that the pseudomorphs consisted in, 100 parts, of—

53·28	insoluble in acetic acid
45·72	soluble „ „ ($CaCO_3$)
0·54	Fe_2O_3
99·54	

and the calculated percentage composition from the results of the analyses made was—

$CaCO_3$.	Fe_2O_3.	SiO_2.	Al_2O_3.	Mn_2O_3.	MgO.	K_2O.	H_2O.
45·72	12·79	28·95	5·72	0·86	0·12	1·83	3·55 = 99·54.

No ferrous oxide could be detected.

The constitution of the pseudomorphous material was about—

46	per cent.	calcium carbonate
13	„	iron-ochre
4·5	„	of a silicate decomposible by hydrochloric acid
10	„	„ „ sulphuric acid
21	„	free uncombined silica;

and this agrees tolerably with the results of the microscpical examination. The silicate soluble in sulphuric acid is, in the opinion of the author, the green amorphous mineral, which cannot be recognised as a definite mineral species, and the same may be said of the other silicate and the minute crystals above referred to. A similar examination of the pseudomorphs, which consisted apparently of iron-ochre, showed their composition to be two-thirds silicates and free silica, the remaining third being iron-ochre, without a trace of calcium carbonate.

The author endeavoured to ascertain the amount of the constituents of the original felspar, which had been lost in the course of the pseudomorphous process. In order to do this it is only necessary to know the *capacity* of the crystal, and the specific gravity of orthoclase (of which the specific gravity and chemical composition vary but little), when the absolute weight of the original orthoclase crystal and its single constituents can be easily calculated. By comparing this weight with the absolute weight of the orthoclase constituents still remaining in the pseudomorphs, the approximate loss is ascertained. It was found that the Meiersgrund pseudomorphs retained their original crystalline form well preserved, and were free from hollow spaces, so that no difficulty was experienced in the weighings. The specific gravity varied from 2·52 to 2·55, thus agreeing closely with that of pure orthoclase, whence the author concludes that these crystals weighed about the same as when fresh; therefore the approximate loss of constituents is obtained by deducting the percentage amounts of the constituents, as found by analysis, still existing in the pseudomorphs, from the percentage normal composition of orthoclase. This method is not applicable, however, to the loosely aggregated pseudomorphs free from calcium carbonate. Assuming the normal composition of orthoclase to be as follows, viz.:—

SiO_2.	Al_2O_3.	K_2O.
65·2	18·1	16·7 = 100·0

and comparing it with the analysis of the pseudomorphs given above, the approximate percentage loss in constituents is as follows:—

SiO_2.	Al_2O_3.	K_2O.
36	12	14

Probable Causes of the peculiar Felspar Decomposition.—The decomposition of felspar crystals above described differs from the ordinary formation of kaolin from felspar, in the fact that a considerable amount of alumina has disappeared in the Meiersgrund crystals, whilst in the kaolin formation, the alumina remains almost without loss, and combined with a portion of the silica. A mechanical removal of silicate of alumina is improbable, owing to the entire absence of that substance in the numerous small veins observed in the rocks already described, and the presence of silica alone in those veins. Probably water containing certain substances in solution brought about the changes observed on the crystals, as both calcium carbonate and ferric hydrate were found in them, and were undoubtedly introduced during the decomposition of the crystals. The author quotes several authorities, von Lasaulx (*Zeitsch. d. deutsch. geol. Gesellsch*, &c., 1873, 330), Cohen (*Porphyre des Odenwaldes*), &c., to show that a loss of alumina has taken place where calcium carbonate and ferric oxide or hydrate occur together in the pseudomorph. Streng (*Jahrb. f. Min.*, 1860, 269), however, gives an analysis of a felspar from the grey porphyry of Elbingerode, in which there is 18 per cent. of calcium carbonate present, and no loss of alumina. Specimens of highly altered or decomposed felspar from the northern slope of the Wilhelmsleite analysed by the author, exhibited a loss of alumina, an entire absence of calcium carbonate, and the presence of a large amount of ferric oxide. In the pseudomorphous pinitoïd after orthoclase, it is well known that a portion of the potash of the orthoclase has been dissolved out and replaced by ferrous oxide and water, but that the amount of alumina still remains unaltered. The author undertook a series of experiments to ascertain the action of calcium and iron compounds upon silicates of alumina, in order to throw some light upon the mode of formation of the Wilhelmsleite pseudomorphs. Bischoff pointed out (*Chem. Geol.*, i, 50) that calcium bicarbonate could be an active agent in the decomposition of minerals, only where a portion of its carbonic acid combined with the alkali of these minerals, thus giving rise to the formation of an insoluble calcium carbonate and a soluble alkaline carbonate, the latter being washed away, and leaving a hollow space in the original mineral. Bischoff states further, that by bringing acid ferrous carbonate and artificially prepared aluminium silicate together, a small quantity of ferric silicate was formed. The author treated finely powdered pure natrolite with a solution of ferrous sulphate for five days, and observed that the powder had assumed a bluish-green colour, and on analysing it and the original pure natrolite he obtained the following results, viz.:—

	SiO_2.	Al_2O_3.	FeO.	Na_2O.	H_2O.	
Natrolite (pure)	47·55	26·60	—	16·36	9·29	= 99·80
„ (treated with $FeSO_4$)	47·02	26·61	2·10	14·99	9·01	= 99·73.

showing that a small quantity of soda has been replaced by ferrous oxide, whilst the amounts of alumina and silica remain unaltered. From this experiment, and the unaltered amount of alumina in the pinitoïd pseudomorphs in presence of ferrous oxide, Dalmer concludes that Bischoff's opinion (that the Meiersgrund pseudomorphs owed their loss of alumina to the action of ferrous bicarbonate) is erroneous. On repeating an experiment of Bischoff's (*Chem. Geol.*, i, 84) in a modified form, the author obtained results showing that under certain conditions ferric hydrate is capable of causing a partial decomposition of aluminium silicate, resulting in the formation of a basic aluminium silicate. Bischoff described the deposit of a spring in the island of Flores, which consisted of silicate of alumina and iron, thus proving that the double silicate is soluble in water. Dalmer heated some finely-powdered scolezite in a flask with ferric chloride solution for some days, at a temperature of 80° C. A stiff reddish-brown mud deposited at the bottom of the flask, which on analysis was found to consist of 50·91 per cent. of silica and 48·03 per cent. of ferric oxide, whilst in the solution filtered off from this deposit, there was a considerable amount of alumina and calcium oxide. This experiment was repeated upon natrolite and analcime, with a similar result, from which it appears that when combined with chlorine, iron is capable of displacing silica and alumina in their combinations, and replacing them in equivalent amounts. This fact is proved in the case of natural minerals, such as the dark-green mesotype of Brevig (Bergmann, *Pogg. Ann.*, 84, 491), and the scapolites of Arendal (vom Rath).

The author concludes by expressing an opinion that ferric hydrate exerted an action upon the aluminium silicate of the original crystal by mechanical contact with it, an opinion which is somewhat confirmed by the yellow colour of the silica particles in contact with the iron-ochre flecks observed in the microscopical examination of thin sections of the pseudomorphs. The experiment made by the author, which has already been alluded to as a modification of one of Bischoff's, appears to strengthen this view. Whether the iron which is dissolved in this experiment is actually combined with the silica and alumina or not is still doubtful. The ferric hydrate found in the pseudomorphs very probably owes its origin to the oxidation of an aqueous solution of acid ferrous carbonate. C. A. B.

Chemical Researches on the Minerals and Rocks of the Island of Vulcano. By A. Cossa (*Gazzetta chimica italiana*, 1878, 235—246).—I. *Potassium-alum containing the Alums of Thallium, Cæsium, and Rubidium.*—The author, in 1873, detected by spectroscopic observation, the presence of thallium in a sample of potassium-alum from Vulcano (Lipari Isles), and in 1877 he showed that this alum contains small quantities of the alums of cæsium and rubidium. A sample of commercial alum from the Vulcano works was found to contain these two metals in quantity sufficient to render their presence visible, without the aid of the spectroscope, by the mere colour which the salt imparted to flame.

The principal deposits of alum in Vulcano are found in the caves of the Faraglione and in the great crater. The Faraglione, also called "Rocca dell alume," is a mass of trachytic rock—decomposed for the most part by sulphuric acid—situated at the southern extremity of the narrow isthmus which joins Vulcanello to Vulcano, and stretching laterally towards the sea. The potassium-alum in its cavities is intimately mixed with aluminium sulphate, gypsum, and sal-ammoniac. In the inner northern wall of the crater of Vulcano there is a rather extensive space called "*la Schicciola*," formed of a white compact rock to which the potassium-alum adheres in layers of various thickness. From several places in this rock there drips a liquid having a strong acid reaction, and dense enough in some parts to form stalactites with concentric zones. In other parts of the same locality, the liquid which drops from the fissures of the rock contains—in addition to potassium-alum—aluminium sulphate and sodium-alum, which, being much more soluble than the potassium-alum, separate from the latter, and collect at the base of the rock in a crystalline mass of very slender needles, forming the outermost layer of the crystalline matter which adheres to the rock. These more soluble salts exhibit here and there a faint yellow tint due to iron-compounds, or a green tint arising from copper. A specimen examined by the blowpipe gave the reaction of cobalt, the presence of which was confirmed by testing in the wet way.

The alum of *la Schicciola*, as it comes from the rock, gives a scarcely perceptible indication of the presence of thallium, even when examined with a good spectroscope, the sodium salt with which it is contaminated interfering with the development of the lines which are characteristic of the other metals; but the less soluble salts, when purified by repeated crystallisation, show distinctly, not only the single green line of thallium, but also the lines α and β of cæsium and rubidium.

The alum obtained from different parts of *la Schicciola* contains various quantities of cæsium and rubidium. The exact amounts have not yet been determined, on account of the difficulty of separating these two metals from potassium, and the still greater difficulty of separating them one from the other. The author is, however, of opinion that, with the exception of pollux, a mineral found in extremely small quantities on the island of Elba, the alum of Vulcano is the richest known source of cæsium and rubidium.

The separation of cæsium from rubidium is most completely effected by Godeffroy's method of precipitation with antimony trichloride from a solution of the two alums in hydrochloric acid, whereby the cæsium is completely precipitated in the form of the double chloride, $SbCl_3.6CsCl$, while the whole of the rubidium remains in solution (*Berlin Berichte*, vii, 375; viii, 9; this Journal, 1876, ii, 272).

Stolba's method of precipitation with stannic chloride (*Dingl. polyt. J.*, cxcvii, 336; cxcviii, 225) does not give good results, the stanno-chloride of rubidium, as well as that of cæsium, being insoluble in strong hydrochloric acid.

To determine whether the rock of *la Schicciola* to which the alum adheres has been simply percolated by a solution of cæsiferous alum, or whether the materials of this alum have been furnished by the decomposition of the rock itself, fragments of the rock, after being repeatedly washed with water to remove the alum, were finely pulverised, and the powder was further washed with boiling water, till the washings, when examined by the spectroscope, gave not the slightest indication of potassium. The remaining powder was then decomposed with a mixture of strong sulphuric and hydrofluoric acid, and the mass was washed with boiling water to remove the greater part of the sulphuric acid, whereby a solution was obtained which, when duly concentrated and left at rest, deposited fine crystals of potassium-alum, the solution of which gave by the spectroscope distinct evidence of cæsium and rubidium. Hence it is highly probable that these two metals existed in the rock in the form of silicates.

The mother-liquors separated from the first crystals of the alum obtained as just described, and containing large quantities of the sulphates of aluminium and sodium, with traces of lithium sulphate, yielded, on addition of sulphuric acid, a precipitate of arsenious sulphide mixed with selenium sulphide. The form in which the arsenic and selenium exist in the rock has not yet been determined.

The rock of *la Schicciola* has a white colour with a slight tinge of yellow, and melts with difficulty, even in thin splinters, producing a white enamel. Its specific gravity at 12° varies from 1·942 to 2·011. It appears to belong to the liparite group, and contains, in the midst of a microfelsitic paste which does not depolarise light, crystals of orthoclastic felspar, some of which are twinned according to the Carlsbad law. The quartz, which is chiefly in the form of tridymite, does not contain any fluid-cavities, but exhibits polyhedral corpuscles. The rock also contains some very small isometric crystals, the mineral species of which has not yet been determined.

Three unaltered lavas from Vulcano, after treatment with sulphuric acid, also yielded crystals of alum containing cæsium and rubidium.

On the edges of a small fumarole at the bottom of the crater of Vulcano, there is found a spongy substance having a crystalline texture, reddish on the surface and dark ash-coloured below. It consists of a mixture of arsenious sulphide, selenium sulphide, boric acid, ammonium chloride, lithium sulphate, thallium- and cæsium-alums, and traces of rubidium- and potassium- alums. On treating it with boiling water, the sulphides of arsenic and selenium separate out, and the slightly concentrated solution soon deposits the sparingly soluble alums of thallium and cæsium.

Another substance, similar to the preceding, excepting in the absence of the sulphides of arsenic and selenium, is still richer in the alums of cæsium and thallium. These two substances would form a source of thallium and cæsium still richer than the alum of *la Schicciola*. In all these porous substances which cover the walls of certain fumaroles, and have the aspect of burnt alum, the quantity of cæsium is much greater than that of rubidium.

Aluminium sulphate mixed with traces of alums, occurs also in the numerous mineral springs which rise up in various parts of the island.

To the south-west of the Faraglione, not far from the works where the boric acid and sulphur are purified, there is a well containing water about a foot and a half deep, from the bottom of which bubbles of gas are continually rising in large quantity, so as to give the water the appearance of boiling. This gas consists chiefly of carbon dioxide, whence the well was called by C. Sainte-Claire Deville, *la Grotta del Cane dell isola di Vulcano.* The following are analyses of the gas by Deville and by Cossa:—

	Deville, 9th July, 1856. Temperature of the gas + 25°.			Cossa, 17th Oct., 1877. Temp. of the water + 22°.		
CO_2..	86·0	83·0	86·0	78·0	—	80·0
O ...	0·4	0·0	0·0	0·5	—	0·6
N ...	13·6	17·0	14·0	21·5	—	19·4
	100·0	100·0	100·0	100·0		100·0

The extraction of alum in the Aeolian Islands, Lipari as well as Vulcano, is an ancient branch of industry, being mentioned by Dioscorides, Pliny, and Diodorus Siculus. The manufacture in Vulcano received a great development in 1813, when the Bourbon Government granted a lease of the crater and its environs to the Nunzianti family of Naples, together with the monopoly of the preparation and sale of the alum throughout the kingdom of the two Sicilies. The mode of extraction then adopted was not limited to the mere lixiviation and crystallisation of the native alum; but the aluminium sulphate occurring together with the potash-alum was mixed with a lixivium of vine-ash,—which is well known to be rich in potash,—also with sal-ammoniac, the product being a mixed alum containing both potash and ammonia. With the abolition of the privilege in 1860, the manufacture soon ceased to be profitable, and after a short time was completely abandoned. (*To be continued.*) H. W.

Lias Rocks of Franconia. By E. v. RAUMER (*Landw. Versuchs.-Stat.*, xxii, 105—128).—The author has made numerous analyses of the lias rocks of the Franconian Jurassic formation.

I. Brown-yellow stone lying midway between limestone and sandstone.

II. The insoluble silicate from I and III, the two analyses combined. The quartz grains are large and milk-white, and they gradually diminish until the sandstone passes into limestone. The latter is in places of pure grey colour, whilst the former shows, in layers, a deep rusty-brown, from the conversion of FeO to Fe_2O_3, as is shown in IV (grey limestone) V (brown-yellow calcareous sandstone, compare I); VI (rusty-brown sandstone). Where this layer comes to the surface, and weathering takes place, the quartz-grains roughen the surface, and the crevices of the rock are filled with a sandy-red clay. The analysis of this rock by Reinsch is given in VIII. The large increase in magnesia is seen only by determining the ration of MgO : CaO (= magnesian quotient).

The ratio of the silicate constituents to the total rock constituents, excluding water, bitumen, and pyrites, gives, according to Neumayr, a means of classifying the rock as 0·0—0·1 limestone, —0·2 marly limestone, —0·4 calcareous marl, —0·6 marl, —0·8, clayey marl, —1·0 clay.

In Schwabia the lower lias is more fully developed; there the rocks agree remarkably well with those under consideration, but appear to be less weathered. IX shows that the fresh rock is almost free from peroxide; whilst X shows the fissured rock; both analysed by Wolf and Wagner (*Würtemb. Jahrshefte*, 1876, 66); both are poor in magnesia.

Next follows a grey friable clay, with ferruginous nodules, of which XI is Reinsch's analysis. Owing to the varying size of the nodules, their great number and soft nature, a selection is difficult to make; but XII, XIII, and XIV are analyses of them, XIII being an analysis of the insoluble silicate, and XIV being made up of XII and XIII. The stone (XV) analysed by Reinsch is more calcareous, but it may have come from a higher level. Compared with the corresponding Schwabian beds, a very marked difference is perceptible; these are calcareous marls with a small amount of magnesia, as is seen under XVI, representing maxima and minima of four analyses by Neumayr, whilst the Franconian beds consist of clay mainly.

The following section consists of grey bituminous, clayey marls, with here and there nests of a kind of clayey coal (XVII). XVIII, XIX and XX give the analyses of this material. Included are layers of a marly limestone (XXI). The marl is interrupted by a yellow bank much richer in lime (XXII), but almost free from bitumen. In Württemberg similar relations are met with; bluish-grey clay (XXIII, Neumayr) and grey limestone (XXIV, Neumayr).

Next is reached the main mass of the Franconian lias. Here are the thick beds teeming with *Posidonia*. Dark-grey, thin, slaty, and tenacious layers, alternate with grey limestone in thin layers, partly rich in *Posidonia Bronni*, and partly full of *Monotis substriata*. The exposed beds have a thickness of about 6 inches. The upper part is given in XXV—XXVII, whilst XXVIII is taken from a lower portion of the section. XXIX is an analysis by Reinsch of a sample from the same section. Under XXX are given the maxima and minima from six analyses by Neumayr, of Schwabian *Posidonia* slates, in which the variation is greater than in the previous one.

The limestone of which XXXI represents an upper variety, and XXXII a lower one, agrees as to its magnesia ratio with the Schwabian (Mg quotient 0·004 and 0·002), but is richer in clay than this, as is shown by the silicate quotient (0·03 and 0·01, Schwabian).

The succeeding Jura marl is not very accessible, being overlaid by a fine-grained Dogger-sandstone. It has been laid bare by the rain in one or two places, but appears to have been intermixed with rock richer in clay. Its analysis is given in XXXIII. The following numbers were obtained by Neumayr (Nm.) and Faist (F.) from Schwabian marl, by von Bibra (v. B.) from Banz, and by Reinsch (R.)

from Moritzberg. Silicate quotient, Nm. 0·14—0·09; F. 0·09—0·09: v. B. 0·15; R. 0·08. Magnesia quotient, Nm. 0·005—0·008; F. 0·017—0·024; v. B. 0·039; R. 0·059.

As a general result the Schwabian and Franconia lias agree very well, both chemically and petrologically, in the Possidonian beds. From this point downwards they deviate more and more.

	I.	II.	III.	XII.	XIII.	XIV.
H_2O	2·85	—	2·85	8·80	—	8·80
SiO_2 insol.	28·29	—	—	81·59	—	—
SiO_2 total	—	96·41	27·54	—	70·31	58·45
SiO_2 soluble	0·06	—	—	0·18	—	—
CO_2	26·82	—	26·82	0·95	—	0·95
HCl	0·02	—	0·02	—	—	—
H_2SO_4	trace	—	trace	trace	—	trace
H_3PO_4	trace	—	trace	0·14	—	0·14
Al_2O_3	0·31	2·47	10·04	1·54	24·37	26·07
Fe_2O_3	9·03			4·04		
FeS_2					0·01	0·01
FeO	1·75	—	1·75	—	—	—
CaO	26·41	0·16	26·46	0·82	0·19	0·97
MgO	3·22	0·02	3·23	0·54	0·67	1·09
K_2O	0·15	0·04	0·16	0·15	1·47	1·37
Na_2O	0·30	—	3·30	0·09	1·08	0·99
	99·21	99·10	99·17	98·84	28·46	98·84
Silicate quotient	0·42	Silicate quot.		0·91		
Magnesia quotient	0·122	Li spectroscopically.			Li in spectr.	
		Magnesia quo.		0·66	6·43	
$\frac{Fe''}{Fe}$	0·177					

	IV.	V.	VI.
Insoluble	4·29	28·29	58·77
SiO_2	3·81	27·54	58·07
Fe, total	7·96	7·68	3·73
Fe''	6·05	1·36	0·24
$\frac{Fe''}{Fe}$	0·760	0·177	0·064

	VIII.		IX.	X.		XI.	XV.
H_2O	6·00	FeO..	1·38	—	H_2O..	14·95	6·96
Insoluble	75·02		17·15	43·28		24·69	74·23
Fe_2O_3	7·72		—	5·89		55·45	8·56
					Al_2O_3.	0·92	3·00
CaO	4·56		43·21	24·14		1·76	2·87
MgO	1·48		0·50	0·34		0·40	1·01
CaO_2	5·22		—	—		1·82	—
	100·00					99·99	100·00
Magnesia quot.	0·324		0·012	0·014			

Silicate quotient.. 0·77
Magnesia quotient 0·35

	XVI.
Insoluble	9·22 —17·48
Fe_2O_3	1·30 — 6·14
FeO	0·34 — 2·20
CaO	41·71 —46·23
MgO	0·08 — 0·39
FeS_2	0·51 — 0·90
Silicate quotient	0·10 — 0·19
Magnesia quotient	0·002— 0·009

	XVII.
H_2O	38·95
H	1·14
C	47·31
Ash	12·60

	XXII.
Insoluble	29·30
Fe_2O_3	2·83
Bitumen	trace
Silicate quotient	0·3

	XVIII.	XIX.	XX.	XXI.		XXV.	XXVI.	XXVII.	XXVIII.
H_2O	9·67	—	9·67	2·78		9·42	—	9·42	25·75
C	0·17	—	0·17	trace		11·00	—	11·00	
					H	0·81	—	0·81	
Insoluble	63·00	—	—	14·59		22·27	—	—	33·97
SiO_2,total	—	68·25	43·55	—		—	67·76	15·28	(23·35)
SiO_2, soluble	0·08	—	—	0·02		0·03	—	—	—
CO_2	7·49	—	7·49	32·15		22·15	—	22·15	15·21
HCl	trace	—	trace	—		0·02	—	0·02	—
H_2SO_4	trace	—	trace	trace		0·04	—	0·04	—
H_3PO_4	—	—	—	Mn_3O_4 0·27	H_2PO_4	trace	—	trace	—
Al_2O_3	3·57	23·33	18·43	3·14		2·39	24·76	9·73	4·76
Fe_2O_3	4·14	2·91	5·98	4·34		1·77			
CaO	9·98	0·23	10·12	41·36		29·38	0·67	29·53	20·04
MgO	0·63	0·31	0·82	0·72		0·41	0·85	0·59	0·27
K_2O	0·18	3·88	2·77	0·14		0·20	2·32	0·72	—
Na_2O	0·12			0·03		0·11	1·27	0·40	—
FeS_2	—	0·04	0·03	—		—	1·40	0·31	—
	99·03	98·95	99·03	99·54		100·00	99·03	100·00	—
Silicate quot.	0·71	—	—	0·15		0·28	—	—	0·45
nesia quot.	0·063	5·94	Li. spr.	0·017		0·014	—	—	0·013

	XXIII.	XXIV.
Insoluble	73·90	9·00
R_2O_3	4·23	2·46
FeO	—	0·47
CaO	5·19	47·56
$CaSO_4$	9·35	—
MgO	0·24	0·28
FeS_2	3·79	0·43
Silicate quotient	0·88	0·09
Magnesia quotient	0·046	0·006

	XXIX.	XXX.		XXXI.	XXXII.
H_2O .... Bitumen	21·13	5·70 —27·20		4·85	8·49
			(SiO_2	—	5·62)
Insoluble......	26·99	24·21 —61·31		5·88	9·05
CO_2..........	18·05	— —		38·22	35·21
Al_2O_3 .... Fe_2O_3	3·75 7·40	2·09 — 4·76	R_2O_3	1·77	1·86
CaO..........	21·63	12·29 —28·22		49·17	45·29
MgO	1·05	0·13 — 1·30		0·11	0·10
FeO..........	—	0·46 — 1·22		—	—
$CaSO_4$........	—	0·75 — 2·94		—	—
FeS_2..........	—	1·23 — 6·88		—	—
$FePO_4$........	—	0·23 — 0·80		—	—
Silicate quot. ..	0·34	0·32 — 0·73		0·06	0·11
Magnesia quot..	0·049	0·005— 0·046		0·002	0·002

	XXXIII.
H_2O..........	8·89
C............	1·15
Insoluble......	55·11
SiO_2, soluble...	0·08
CO_2..........	11·24
HCl..........	trace
H_2SO_4........	—
H_3PO_4........	trace
Sl_2O_3	3·11
Fe_2O_3	4·46
CaO..	14·98
MgO	0·17
K_2O..........	0·13
Na_2O	0·08
	98·59
SiO_2, total	36·98
Silicate quot. ..	0·60
Magnesia quot..	0·011

J. T.

On a Fourth Mass of Meteoric Iron from Augusta Co., Virginia. By J. W. Mallet (*Amer. J. of Sci.* [3], xv, 337).—This meteorite was found about 1858, at Staunton, Augusta Co., whence three other similar meteorites have been obtained (*ibid.* [3], ii, 10). In shape it is like many metallic meteorites, being irregularly rounded, larger at one end than the other, with well marked concave depressions. Its length is 45·7 cm.; width, 29·2 cm.; and thickness, 20·3 cm.; weight = 152 lbs. Magnetic polarity was detected at various points. Sp. gr. = 7·888 at 18°. The iron is compact and crystalline, with plates of schreibersite running through it, and a few specks of troïlite. The Widmanstättian figures were clearly brought out by nitric acid. Analysis:—

Fe.	Ni.	Co.	Cu.	P.	S.	C.	Si.
91·439	7·559	0·608	0·021	0·068	0·018	0·142	0·108 = 99·963.

Traces of tin and chlorine were also found, the chlorine existing as ferrous chloride.

C. W. W.

Composition of the Rivers Parana and Uruguay. By J. J. Y. Kyle (*Chem. News*, xxxviii, 28).—The Rio de la Plata, or River Plate, in reality the estuary of the rivers Parana and Uruguay, is characterised by its muddy appearance, and always contains in suspension a considerable amount of "colloïd" clay, derived from the immense territory drained by the river Parana. The Uruguay is a river remarkable for its transparency and freedom from suspended matters. The following table shows the proportion and composition of the residue yielded by 1000 c.c. of each of the three waters:—the River Plate, at about five miles above the city of Buenos Ayres; the Parana, at about five miles above its termination in the Plate; and the Uruguay, in the middle of its stream, in front of the town of Salto, in the republic of Uruguay:—

	River Plate. grm.	River Parana. grm.	River Uruguay. grm.
Sodium oxide..........	0·0212	0·0189	0·0020
Potassium oxide........	0·0034	0·0046	0·0015
Calcium ,, ...	0·0078	0·0095	0·0055
Magnesium ,, ...	0·0050	0·0043	0·0019
Iron ,, ...	0·0040	0·0030	—
Aluminium ,, ...	0·0060	0·0030	—
Silica (SiO_2)..........	0·0193	0·0194	0·0185
Sulphuric acid (SO_3) ..	0·0058	0·0079	0·0013
Carbonic acid (CO_2)....	0·0116	0·0122	0·0071
Chlorine..............	0·0114	0·0149	0·000247
Nitric acid (N_2O_5)......	—	—	0·0019
Organic matters........	0·0100 ?	0·0106 ?	traces
	0·1055	0·1083	0·039947
Determined directly....	0·1000	0·1000	0·039500

The three waters were examined by Wanklyn's process, and yielded per liter:—

	mgrm.	mgrm.	mgrm.
Free ammonia	0·07	0·16	0·07
Albuminoïd ammonia...	0·24	0·24	0·10
Hardness (1° = 0·01 grm, per liter of $CaCO_3$) ..	4·00°	4·50°	2·25°

The waters of both the Plate and Parana always yield by Wanklyn's process a very large amount of albuminoïd ammonia, derived chiefly from vegetable organic matters, partly in solution and partly adherent to the suspended clay. In spite of this and its opaline, sometimes even muddy appearance, the Plate water is highly esteemed as a drinking water. The river Uruguay is probably one of the purest river waters in the world, containing rather less than 4 parts of solid matter in 100,000. It is almost free from chlorides; the determination made with every possible care, gave rather less than one-fourth of a milligram per liter, and this, be it remembered, at a distance of say 500 miles from its source. Still more noteworthy is the fact that about 46 per cent. of the total solid matter consists of soluble silica, not suspended as in the other two rivers. A small proportion exists, probably as alkaline silicate, but the greater part is undoubtedly present as hydrated silicic acid. To this circumstance may be found an explanation of the petrifying properties attributed to the water of the Uruguay. D. B.

Organic Chemistry.

Action of Steam on Red-hot Charcoal. By J. H. LONG (*Liebig's Annalen*, cxcii, 288—295).—A series of samples of the mixture of gases produced by passing steam over charcoal heated to redness in a porcelain tube, were analysed by the author. He found that as the operation proceeded, each successive sample contained an increased proportion of carbon dioxide, and a diminished amount of the monoxide. From the 1st to the 7th sample analysed, the percentage in volume of carbon dioxide gradually increased from 19·92 to 30·93, whilst that of the monoxide decreased from 26·91 to 3·95. The proportion of hydrogen by volume increased at the same time from 52·91 to 64·87. These variations are attributed to the gradual removal of the excess of charcoal, which the author thinks is probably first oxidised into carbon dioxide, a part of which is reduced by the excess of carbon into carbon monoxide, and this last substance partially enters into a third reaction with the steam, thus:—$CO + H_2O = CO_2 + H_2$. R. R.

Decomposition of Petroleum by Heat. By A. LETNY (*Deut. Chem. Ges. Ber.*, xi, 1210—1212).—Petroleum (sp. gr. 0·87, b. p. 270°), when passed in large quantities through a wide iron tube filled with coke, and heated to redness, yields water, benzene, toluene, xylene, cumene, naphthalene, phenanthrene, and anthracene. With a narrower tube, and a smaller quantity of petroleum, no solid products are obtained, but only benzene, toluene, xylene, cumene, and very small quantities of amylene, hexylene, and heptylene. T. C.

Hexylenes. By JAWEIN (*Bull. Soc. Chim.* [2], xxx, 26).—Of the three hexylenes indicated by theory, one has been described by Pavloff, who assigns to it the formula $(CH_3)_2C{:}C(CH_3)_2$; the two others, derived from diethylmethylcarbinol and from dimethylpropylcarbinol, have respectively the constitutions, $CH_3.CH{:}C(CH_3).C_2H_5$, and $(CH_3)_2C{:}CH.C_2H_5$; the first boils at 69—71°; the second at 65—67°. The condensation of these two hexylenes appears to take place in the same way as that of isobutylene by dilute sulphuric acid. The product of the condensation of the hexylene $(CH_3)_2C{:}CH.C_2H_5$, boils at 193—197°, whilst that of $CH_3.CH{:}C(CH_3).C_2H_5$, boils at 196—199°; these products are probably isomeric, and not identical, a question which the author proposes to settle by further investigation. C. W. W.

Oxidation of Hexylene from Mannite. By O. HECHT (*Deut.

Chem. Ges. Ber., xi, 1152—1154).—Chapman and Thorpe found (*Annalen*, cxlii, 182) that β-hexylene from mannite gave on slow oxidation by chromic acid, carbonic, acetic, and propionic acids. The author has repeated this experiment, and has obtained besides carbonic and acetic acids, normal butyric, and not propionic acid, the only difference in the conditions being that Chapman and Thorpe treated the hexylene with moderately dilute chromic acid solution in sealed tubes at 100°, whilst in the present case a concentrated chromic acid solution was employed, and the reaction carried on at the boiling point of hexylene in a flask with reversed condenser. This difference in the manner of working could, however, have no influence on the result. The reaction is as follows:—

$$C_6H_{12} + 4O = C_2H_4O_2 + C_4H_8O_2.$$

The carbonic acid is due to the further oxidation of a portion of the butyric acid (*Ber.*, xi, 1050). Special experiments were made to show that the action of the sulphuric acid on the hexylene was not such as to form secondary hexyl alcohol, and the latter its well known oxidation products.

From the foregoing results, as well as those on the oxidation of hexylene glycol (see this vol., p. 966), the following constitution is ascribed to Erlenmeyer and Wanklyn's hexylene,

$$CH_3.CH{=}CH.CH_2.CH_2.CH_3,$$

or that of normal propylmethylethylene; hexylene bromide and glycol are therefore $CH_3.CHBr.CHBr.CH_2.CH_2.CH_3$, and $CH_3.CH(OH).CH(OH).CH_2.CH_2.CH_3$ respectively.

T. C.

Oxidation of Diallyl. By Sorakine (*Bull. Soc. Chim.* [2], 24).—By the oxidation of diallyl the author obtained acetic acid as well as carbonic acid, a result which he thinks is difficult to understand if the formula of diallyl be taken as—

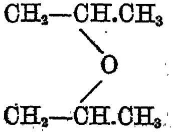
$$CH_2{=}CH.CH_2.CH_2.CH{=}CH_2.$$

C. W. W.

Constitution of Diallyl. By L. Henry (*Bull. Soc. Chim.* [2], xxx, 50).—The author considers that the formation of acetic acid by the oxidation of diallyl with sulphuric acid and potassium dichromate, is not inconsistent with the formula $CH_2{=}CH.CH_2.CH_2.CH{=}CH_2$. It is known indeed that the group $CH_2.CH$— of propylene, when subjected to the successive action of sulphuric acid and water, takes up the elements of water, forming $CH_3.CH(OH)$—; the author therefore considers that diallyl or dipropylenyl, which contains the propylene group, will act in the same way, forming

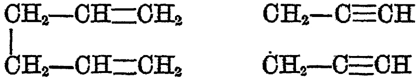
$$CH_3.CH(OH).CH_2.CH_2.CH(OH).CH_3,$$

which, by losing one molecule of water, forms



hexylene oxide (Jekyll, *Zeit. für. Chem.*, vii, 36), and it is this latter body which furnishes the acetic acid by oxidation. It may be observed in support of this view, that the oxidation of diallyl by nitric acid does not furnish any acetic acid.

The formation of dipropargyl, C_6H_6, from diallyl is easily explained by the ordinary formula of diallyl, but by no other.



$$\begin{array}{ll} CH_2{-}CH{=}CH_2 & CH_2{-}C{\equiv}CH \\ | & | \\ CH_2{-}CH{=}CH_2 & CH_2{-}C{\equiv}CH \end{array}$$

Diallyl. Dipropargyl.

C. W. W.

Action of Tertiary Butyl Iodide on Isobutylene in presence of Calcium Oxide. By JULIE LERMONTOFF (*Bull. Soc. Chim.* [2], xxx, 21).—In this reaction two hydrocarbons, isodibutylene and isotributylene are formed according to the following equations, $C_4H_8 + C_4H_9I - HI = C_8H_{16}$, and $C_8H_{16} + C_4H_9I - HI = C_{12}H_{24}$.

The identity of these hydrocarbons with those which Butlerow obtained by the condensation of isobutylene was proved by their boiling points, densities, and products of oxidation.

The action of tertiary butyl iodide on isodibutylene, in presence of lime, produces an isotributylene identical with the above, showing that it is not formed according to the equation $C_4H_8 + 2C_4H_9I - 2HI = C_{12}H_{24}$. C. W. W.

On Vinyl Bromide. By LIVOFF (*Bull. Soc. Chim.* [2], xxx, 25).—Pure vinyl bromide boils at 15—16°. Its polymerisation takes place most readily under the influence of the more refrangible rays of the spectrum, and is effected more easily in the liquid than in the gaseous state. The polymeride is easily soluble in methyl iodide and similar iodides, in bromoform, benzoic aldehyde, and aniline. Nitric acid gives an amorphous nitrobromo-compound soluble in alcohol; hydriodic acid, at 150°, gives a substance melting at about 100°, nearly insoluble in alcohol and ether. C. W. W.

New Mode of Preparation of Allyl Bromide. By H. GROSHEINTZ (*Bull. Soc. Chim.* [2], xxx, 98).—Bromide of potassium is heated with sulphuric acid diluted with its own volume of water in a flask furnished with a condenser, and as soon as hydrobromic acid comes off, allyl acohol is allowed to drop into the flask; the allyl bromide then distils over with vapour of water, and may be purified by washing with alkaline water and drying with calcium chloride. The preparation is easy and rapid, and the product satisfactory.

C. W. W.

Preparation of Trimethylene Bromide. By BOGOMOLETA (*Bull. Soc. Chim.* [2], xxx, 23).—The best way of preparing this compound is to heat allyl bromide in sealed tubes for 3—4 hours at 150° with half its weight of fuming hydrobromic acid. The transformation is complete, and the product perfectly pure.

The author did not obtain good results by Reboul's method, which consists in saturating allyl bromide with gaseous hydrobromic acid at 0°. C. W. W.

On Ethylene Cyanide. By M. NEVOLÉ and J. TCHERNIAK (*Compt. rend.*, lxxxvi, 1411—1413).—Ethylene cyanide was prepared in quantity with the intention of changing it by reduction into normal butylene-diamine, and transforming this by the action of nitrous acid into the corresponding glycol. Although Fairley's process of reduction by tin and hydrochloric acid was found to be unsatisfactory, yielding mere traces of the diamine, the authors succeeded in rendering the preparation of ethylene cyanide more easy, and in obtaining it perfectly pure by the following process:—A mixture of 150 grams of ethylene bromide with 117 grams of 90 per cent. potassium cyanide was made semifluid by addition of alcohol, and heated on a water-bath for 20 hours, the whole being occasionally shaken. Several such batches were united and distilled in a vacuum by the heat of an oil-bath. As soon as the distillate began to solidify, the receiver was changed, and a colourless oil passed over under a pressure of 4 or 5 mm. and at 140—160°, which rapidly solidified to a colourless mass. This product was separated from a little ethylene bromide by solution in water, and on evaporation of the water a brilliant white amorphous substance was obtained, which melted at 54·5° and resolidified at 53°. It was found to be very soluble in water, alcohol, and chloroform, but only slightly soluble in carbon bisulphide. This substance was proved by analysis to be perfectly pure ethylene cyanide: it differs in its properties as given above from the product obtained by Maxwell Simpson, who described it as slightly brown and *crystalline*. F. C.

Researches on Azotised Acids derived from the Ketones. By G. CHANCEL (*Compt. rend.*, lxxxvi, 1405—1408).—The paper is an attempt to fix, from a consideration of recent researches, the chemical constitution of an acid formerly obtained by the author from butyrone by the action of nitric acid. The author no longer considers it to be nitropropionic acid, as was originally suggested and apparently confirmed, as it possesses neither the composition nor properties of that acid. The name *propylnitrous acid* is recommended as implying its constitution, its relation to propionic acid, and its mode of decomposition. Analyses give for the acid the formula of dinitropropane, $C_3H_6(NO_2)_2$, and its silver, potassium, and ammonium salts have formulæ in which one atom of hydrogen is replaced by one atom of the metal. The author considers this body to be identical with the dinitropropane prepared by ter Meer by the synthetical methods of Victor Meyer. He does not agree, however, with the constitution hitherto assigned to it, in which two NO_2 groups are directly combined with C, but thinks that either two O.NO groups, or a diatomic complex group containing N_2O_4 must be united to the carbon atom. Victor Meyer has proved satisfactorily that the group NO_2 is present in the monobromonitropropane from which ter Meer's preparation was made, but the author submits that treatment with alcoholic potash may be able to change the group NO_2 into O.NO. The constitution suggested above would explain the ready evolution of nitrogen from the ammonium salt, *i.e.*, from ammoniumpropyl nitrite, also the conversion of the acid under the action of nascent hydrogen in acid solutions into propionic acid and hydroxylamine. The acid when distilled with dilute sulphuric acid splits up into nitrogen dioxide and propionic acid. The other ketones, when treated with nitric acid, behave like butyrone; and in the case of mixed ketones the higher alcohol-radicle seems to undergo the double nitrous substitution. F. C.

Ethylidenimido-silver Nitrate. By A. GOLDSCHMIDT (*Deut. Chem. Ges. Ber.*, xi, 1198—1201).—This is a continuation of Liebermann's work on the same subject.

Ethylidenimido-silver nitrate, $2(C_4H_{10}N_3O_3Ag) + H_2O$, separates out slowly in the form of pearly plates when silver nitrate is carefully added to a mixture of ½ vol. ammonia with an alcoholic solution of 1 vol. of aldehyde, without shaking the vessel. It can also be obtained in monoclinic crystals by evaporating the ammoniacal solution over sulphuric acid in a vacuum. It loses its water of crystallisation over sulphuric acid, and blackens on heating to 100°. It appears to be identical with the ethylidenargentamine-ethylidenammonium nitrate described by Mixter (*Amer. Jour. Sci.*, Sept., 1877), who ascribed to his compound, however, the formula, $8(C_4H_{10}N_3O_3Ag) + 5H_2O$.

Valerianic and formic aldehydes give similar compounds, both of which are very readily decomposed. T. C.

Action of Chlorine on the Nitroprussides under different Circumstances. By E. W. DAVY (*Chem. News*, xxxviii, 105).—It is stated in the different standard works on chemistry that chlorine has no action on the nitroprussides; but the author found this not to be the case, at least as regards many of those salts which he made the subject of experiment. Although chlorine does not appear, under ordinary circumstances, to produce any immediate action, still, when its operation is long continued, it effects a very slow decomposition. If, however, its action is assisted by the agency of sun-light, it operates much more quickly and soon produces the complete decomposition of those salts. The author's experiments in this direction were chiefly made on the sodium nitroprusside, which, on exposure to chlorine and the action of strong sun-light, was decomposed into the compound known under the name of chlorocyanic oil, $(C_6N_4Cl_{14})$, ferric chloride, sodium chloride, and hydrochloric acid. The potassium, barium, calcium, zinc, iron, manganese, and silver salts were attacked in a similar manner, the copper salt being the only one of those compounds which resists the combined action of light and chlorine. Heat, like light, appears to aid the decomposing action of chlorine on the nitroprussides. D. B.

Propylglycol. By FLAVITZKY (*Bull. Soc. Chim.* [2], xxx, 22).—Propylglycol, prepared from pseudopropyl iodide, boils at 185·3° (188—189°, Wurtz); its sole product of oxidation is acetic acid. The author's supposition that the primary-secondary glycols produce by their dehydration a ketone as well as an aldehyde, is not borne out in the case of propylglycol; the action of zinc chloride and of sulphuric acid produce only propionic acid and aldehyde. C. W. W.

Action of Dilute Sulphuric Acid on Tetramethylethyleneglycol. By PAVLOFF (*Bull. Soc. Chim.* [2], xxx, 26).—Tetramethylethyleneglycol (synthetic pinacone) heated with dilute sulphuric acid gives pinacolin, which produces trimethylacetic acid by its oxidation. These facts, joined to the identity of crystalline form and melting point of ordinary pinacone hydrate with those of tetramethylethyleneglycol, leave no doubt as to the constitution of pinacone.

C. W. W.

Oxidation of Hexylene Glycol from Mannite. By O. HECHT and J. MUNIER (*Deut. Chem. Ges. Ber.*, xi, 1154—1155).—The glycol employed was obtained from hexylene bromide (from mannite), partly by Wurtz's method and partly by a modification of that of Zeller and Hübner; in the latter case 20 grams of bromide were treated, in a flask with reversed condenser, with 11·5 grams of potassium carbonate and 140 grams of water, a little very dilute potassic hydrate being added from time to time. When nearly all the bromide had dissolved, carbonic acid was passed in to saturate free alkali, and the liquid, after separation from undissolved bromide, was shaken with potash, and the glycol dissolved out by ether; 2·5 grams of pure glycol were thus obtained.

Hexylene glycol (b. p. 203—210°) on oxidation by dilute chromic acid solution gave carbonic, acetic, and normal butyric acids; a smell of acroleïn was also evolved, probably as an intermediate product of oxidation. The reaction may be represented thus: $C_6H_{14}O_2 + O_3 = C_2H_4O_2 + C_4H_8O_2 + H_2O$. The carbonic acid was due to further oxidation of part of the butyric acid.

T. C.

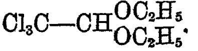
Action of Fused Potash on Glycerin. By E. HERTER (*Deut. Chem. Ges. Ber.*, xi, 1167—1168).—The author finds that, besides the acetic and formic acids obtained by Dumas and Stas (*Ann. Chim. Phys.*, lxxiii, 148), and the acrylic acid by Redtenbacher, butyric and fermentation lactic acids are also produced by the action of fused potash on glycerin, thus: $C_3H_8O_3 + KHO = C_3H_5KO_3 + H_2O + H_2$, the formation of butyric acid being apparently due to the further decomposition of the lactic acid by the potash (Seyler, *Zeit. f. Phys. Chem.*, ii, 14).

T. C.

Action of Hydrochlorides of the Amines on Glycerin. By J. PERSOZ (*Compt. rend.*, lxxxvii, 31).—The author having been engaged upon these investigations since 1875, desires to claim priority of publication for them, inasmuch as M. Hanriot has recently presented a communication on the same subject. The method of operating consists in heating glycerin directly with the hydrochlorides of amines and diamines, more particularly with those belonging to the aromatic group. Thus, when glycerin is heated with aniline, phenyl-derivatives of glyceramine are obtained, together with secondary products.

J. W.

Trichloracetal. By H. BYASSON (*Compt. rend.*, lxxxvii, 26).—When chlorine acts on alcohol at 75°, the principal products formed are chloral alcoholate, chloral hydrate, ethyl chloride, hydrochloric acid, and especially trichloracetal. 500 litres of alcohol in this manner yielded, after many fractionations, one litre of trichloracetal,



$Cl_3C—CH\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}.$

Trichloracetal is a transparent liquid of peculiar odour, boiling at 197°. Its density is 1·288. Water dissolves scarcely 5 grams per litre, but it is freely miscible with alcohol, ether, glycerin, &c. Heated with sulphuric acid, it is decomposed into anhydrous chloral which volatilises whilst the acid blackens, owing to some secondary decomposition. 500 grams of trichloracetal heated with 1,500 grams of oil of vitriol gave 328 grams of chloral instead of the theoretical quantity, 333 grams. Hot alkali does not attack it, but nitric acid at 80° attacks it violently with formation of trichloracetic acid and other products. J. W.

Supposed Compounds of Grape Sugar with Cupric Hydrate. By W. MÜLLER and J. HAGEN (*Pflüger's Archiv. f. Physiologie*, xvii, 568—589).—Salkowski (*ibid.*, vi, 220) obtained a compound of grape sugar and cupric hydrate, containing 5 molecules of the latter to 1 molecule of the former body, by mixing solutions of grape sugar, cupric sulphate, and sodium hydrate in certain proportions; complete precipitation of the cupric hydrate and of the sugar was accomplished only when the proportion of sugar, cupric sulphate, and sodium hydrate was exactly as 1 : 5 : 10 molecules. The authors have repeated and modified Salkowski's experiments. The solutions of sugar (0·9 gram), cupric sulphate, and sodium hydrate were cooled and mixed in a vessel surrounded by ice; the precipitate contained the whole of the copper, and about 90 per cent. of the sugar originally employed. On washing repeatedly with ice-cold water, about 12 per cent. of sugar was removed from the precipitate. The proportion of cupric hydrate retained by 1 molecule of sugar varied in different experiments from 6·48 to 7·35 molecules. The authors believe that Salkowski obtained his results by working with diabetic urine; they themselves employed perfectly pure grape sugar.

The generally accepted rationale of Trommer's sugar test, viz., the production of a compound of 1 molecule of sugar and 5 molecules of cupric hydrate, and the subsequent solution of this compound in the excess of potash used, is regarded by the authors as incorrect. Analysis of the precipitate containing sugar and cupric hydrate showed that the composition of this substance varied considerably: hence it could not be a definite compound. On account of the partial decomposition of the sugar, even at very low temperatures, and in spite of special precautions, it was difficult to gain definite information with regard to the exact nature of this precipitate; but the facts, that after being washed until the washings ceased to contain sugar, the precipitate yielded sugar to water when suspended in the liquid, and that a mixture of 1 molecule of sugar with 30 molecules of cupric sulphate, and 60 molecules of sodium hydrate, yielded a precipitate, the filtrate from which yet contained sugar, prove, in the authors' opinion, that no definite chemical compound of grape sugar and cupric hydrate is produced in these experiments.

The authors have also attempted to prepare a compound of grape sugar and cupric oxide by dissolving cupric hydrate in a solution of sugar, but without success.

Hoppe-Seyler (*Handb. d. Physiol. u. Pathol. Chem. Anal.*, 1870, p. 108) asserts that a solution of grape sugar dissolves cupric hydrate, forming an unstable solution, from which cuprous oxide speedily separates, the sugar being oxidised to formic and other acids, and to a dextrin-like body. By careful and repeated experiments with cupric hydrate freshly precipitated, both dried in air and moist, the authors have assured themselves that this compound is altogether insoluble in a solution of pure grape sugar.

Fileti's (*Deut. Chem. Ges. Ber.*, viii, 441) copper glucosates are asserted by the authors to be really compounds containing sugar, cupric oxide, and potassium. (*See the following abstract.*)

M. M. P. M.

Compounds of Grape Sugar with Cupric Oxide and Potassium. By W. MÜLLER and J. HAGEN (*Pflüger's Archiv. f. Physiol.*, xvii, 601—616).—Peculiarities in the phenomena exhibited in carrying out Trommer's sugar-test, as noted by Reichardt (*Annalen*, cxxvii, 299) induced the authors to study the behaviour of grape sugar towards cupric hydrate in alkaline liquids. Grape sugar and potassium hydrate solutions were mixed in definite proportions, and a measured amount of a solution of cupric sulphate was added, the whole being surrounded by ice. The following table represents the number of molecules of cupric hydrate dissolved by 1 molecule of grape sugar, in presence of a varying number of molecules of potassium hydrate.

1 molecule of grape sugar in presence of—

1 molecule of potassium hydrate dissolves 1 to 1·5 molecules of cupric hydrate.
2·5—3 molecules of potassium hydrate dissolves 1·75 molecules of cupric hydrate.
4 molecules of potassium hydrate dissolves 2 molecules of cupric hydrate.
5 molecules of potassium hydrate dissolves 2·5 molecules of cupric hydrate.
6—10 molecules of potassium hydrate dissolves 2·75 molecules of cupric hydrate.

With a large excess of potassium hydrate 2·75 molecules of cupric hydrate only were dissolved. Inasmuch as 1 molecule of grape sugar is capable of reducing 5 molecules of cupric oxide in hot alkaline solution, it follows that this sugar can dissolve a much smaller amount of cupric hydrate than it can reduce; it is not therefore necessary, in performing Trommer's sugar test, to cease adding cupric sulphate when the precipitate is no longer redissolved.

By varying their experiments, viz., by mixing solutions of sugar and cupric sulphate, and then adding potassium hydrate, the authors found that, in presence of 8—10 molecules of the latter salt, 1 molecule of sugar was capable of dissolving 3 molecules of cupric hydrate; and of dissolving 3·5 molecules of the same hydrate when 13—33 molecules of potassium hydrate were present.

Pursuing the process used by Fileti in preparing the so-called copper glucosates (*Ber.*, viii, 441), the authors have obtained a substance which they regard as a compound of 1 molecule of sugar, 1 atom of copper, and 1 atom of potassium; and by using cupric acetate instead of sulphate, they have obtained a compound containing 2 atoms of copper, 1 atom of potassium, and 1 molecule of sugar. These substances are soluble in water. Experiments have shown that no corresponding *insoluble* double salt exists, but that the permanent precipitate produced, by adding 4 to 5 molecules of cupric sulphate to 1 molecule of sugar, in a solution containing excess of alkali, consists only of cupric hydrate.

M. M. P. M.

Composition of Honey. By J. C. BROWN (*Analyst*, 1878, 267).—The following table gives the results of the analysis of authentic specimens of honey from various sources:—

	English.	Welsh.	Normandy.	German.	Greek.	Lisbon.	Jamaica.	California.	Mexican.
Water expelled at 100°	19·10	16·40	15·50	19·11	19·80	18·80	19·46	17·90	18·47
Water expelled at a high temperature and loss	7·60	6·56	4·95	11·00	7·80	6·66	7·58	8·13	10·03
Levulose	36·60	37·20	36·88	33·14	40·00	37·26	33·19	37·85	35·96
Dextrose	36·55	39·70	42·50	36·58	32·20	34·94	35·21	36·01	35·47
Cane-sugar (?)	doubtful	—	—	—	—	1·20	2·20	—	doubtful
Wax, pollen, and insoluble matter	trace	trace	trace	trace	0·05	1·00	2·10	trace	trace
Mineral matter...	0·15	0·14	0·17	0·17	0·15	0·14	0·26	0·11	0·07

The specific gravity of honey is about 1·41, but varies slightly with the proportion of water.

A solution of 16·26 grams of crude honey in 100 c.c. water produces a deviation of −3·2° to −5° at 60° F. Greek honey produces a deviation of −5·5°. The same weight of dried honey in 100 c.c. water gives a deviation of about −4·8°.

C. W. W.

Isodulcite. By R. S. DALE and C. SCHORLEMMER (*Deut. Chem. Ges. Ber.*, xi, 1197—1198).—Isodulcite, when heated with concentrated hydriodic acid, is in great part converted into a tarry mass, whilst at the same time a heavy liquid containing iodine distils over. This liquid consists of a mixture of bodies, none of which the authors have been able to obtain in the pure state.

T. C.

Action of Diastase on Starch. By MAERCKER (*Landw. Versuchs.-Stat.*, xxii, 69).—Musculus asserts that 3 parts of starch yield 2 of dextrin and only 1 of sugar, whilst Schwarzen's results, confirmed by the author, obtained at the temperature of 48° R., showed 1 of sugar to 1 of dextrin. This sugar is not dextrose but maltose, which has only two-thirds the reducing power of the former, and as half the reducing power of the product resulting from the action of diastase on starch is due to maltose, the 4 starch-groups must yield 3 of maltose and 1 of dextrin. At higher temperatures varying results have been obtained. At 65°, the yield of maltose is lowered by several per cent.; at a still higher temperature, a tolerably constant relation holds between the maltose and dextrin (2 starch give 1 maltose and 1 dextrin). Possibly there are two diastase ferments, one of which produces much maltose and little dextrin, but is destroyed while the temperature is still comparatively low; while the other, destroyed at higher temperatures only, produces less maltose and more dextrin. The second diastase ferment appears not to act upon dextrin, whilst fresh unwarmed diastase readily converts the dextrin into sugar. The action of acids on diastase is similar to that of heat: in small quantity they act like a temperature of 52—56° R. (more dextrin formed), whilst more acid entirely stops the action. J. T.

Identity of Inulin from different Sources. By LESCŒUR and MORELLE (*Compt. rend.*, lxxxvii, 216—217).—Inulin has been prepared from elecampane, dahlia, and chicory, and contrary to the statement of Ferrouillat and Savigny (*Compt. rend.*, lxviii, 1571) the authors find that from whatever source inulin is obtained, it is identical in chemical and physical properties.

Inulin which had been prepared in the same manner from elecampane, dahlia, and chicory, gave with Laurent's polarimeter a rotary power in which $a_D = -36{\cdot}56, -36{\cdot}57, -36{\cdot}18$ respectively.

Its acetic acid derivatives, obtained by the action of acetic anhydride, also correspond in character and composition; compounds have been obtained of the formulæ—

$$C_{12}H_{14}O_7(C_2H_4O_2)_3;\ C_{12}H_{12}O_6(C_2H_4O_2)_4;\ C_{12}H_{10}O_5(C_2H_4O_2)_5.$$

Inulin also plays the part of a weak acid, forming with alkalis compounds which are soluble in water, but precipitated therefrom by alcohol. These compounds are amorphous, viscid, and translucent; they are unstable, as from their solution in water inulin is again precipitated on adding more water, or on passing carbonic anhydride through the solution.

Sodic inulate has a rotary power = −33°. A. J. C.

Action of Ammonia on Ethylic Aceto-acetate. By H. PRECHT (*Deut. Chem. Ges. Ber.*, xi, 1193—1195).—Diphenylurea is obtained by the action of aniline on ethylic aceto-acetate; neither gaseous, aqueous, or alcoholic ammonia, however, produces urea by an analogous reaction, but yields a liquid product, one half of which distils at 200—210°, whilst the residue consists of a syrupy mass, which becomes crystalline after a few weeks. By recrystallisation from alcohol, solution in alkalis, and reprecipitation by acids, a crystalline acid containing nitrogen was obtained, but was not further investigated. On passing perfectly dry ammonia into ethylic aceto-acetate kept cool by ice, nearly one molecule of the gas was absorbed, crystals soon began to separate, and at the end of the reaction, the whole solidified to a white crystalline mass. Different preparations of these crystals, however, showed no constant melting point; one sample melted at 37°, and the others at lower temperatures. By fractional fusing and taking that portion melting first, crystals were obtained, which melted at 27°, and dissolved in alcohol and ether in all proportions, but were insoluble in water. They changed at the ordinary temperature into a colourless liquid, which sank under water, and solidified at 3°. Analysis led to the formula $C_6NH_{11}O_2$. The author considers it to be an amide, and represents its formation by the equation: $C_6H_{10}O_3 + NH_3 = C_6NH_{11}O_2 + H_2O$. This substance is isomeric, but not identical with Geuther's ammonium ethylene-dimethylene carbonate (*Archiv. der Pharm.*, cxxv, 29, 201; *Jahrsb.* (1875), 302); for Geuther's compound is soluble in water, can be sublimed, and melts above 63°, whilst the compound just described is insoluble in water, and is decomposed on heating. T. C.

Diehic Acid, a New Acid obtained by the Action of Potassium Permanganate on Sugar. By E. Maumené (*Bull. Soc. Chim.* [2], xxx, 99).—The author has already described two acids, hexepic and triepic, formed by the action of permanganate on sugar; the present acid is more easily obtained than these two. Its potassium salt crystallises remarkably well; its solution does not precipitate metallic solutions, but the neutral lead salt reduces solutions of gold and silver, and forms double salts. Its formation is represented by the simplified equation, $C_{12}H_{22}O_{11} + 3K_2Mn_2O_8 = 6C_2H_3KO_4 + 3Mn_2O_3 + 2H_2O$, but this equation, as indicated by the author's theory, is never actually realised.

Diehic acid, $C_2H_4O_4$, may be considered as acetic (diedic) acid, $C_2H_4O_2 + O_2$, corresponding to dihydrodedic acid, $C_2H_8O_2$, which is acetic acid $C_2H_4O_2 + H_4$. C. W. W.

New Method of Preparing Ethyl Glycollate. By T. H. Norton and J. Tcherniak (*Compt. rend.*, lxxxvii, 30).—Glycollide and absolute alcohol in equivalent proportions are heated together in a sealed tube at 200°, until the glycollide has entirely disappeared. The contents of the tube are then treated with a saturated solution of potassium carbonate to separate the ether, which may be dried and rectified. The theoretical yield of ethyl glycollate, boiling at 155°, was thus obtained.

It is thought probable that mercaptan would react with glycollide in a similar manner, producing an ether of thioglycollic acid, $CH_2.OH.CO.SC_2H_5$. J. W.

Ethoxy-acetonitril. By T. H. Norton and J. Tcherniak (*Compt. rend.*, lxxxvii, 27—29).—All attempts to dehydrate glycollamide, so as to obtain the corresponding nitril, having failed, it was thought that possibly the reaction might succeed with ethyl-glycollamide, inasmuch as phosphoric anhydride is known to be without action on the group ethoxyl, while it acts energetically and in a manner but imperfectly understood on bodies containing the group hydroxyl.

Monochloracetic acid was therefore converted successively into ethyl-glycollic ether and ethyl-glycollamide, and the latter was afterwards distilled with phosphoric anhydride. 40 grams of the amide mixed with 60 grams of anhydride gave, on distillation on a sand-bath, a product boiling between 132° and 134°, which after two rectifications weighed 15 grams. Analysis showed it to be nearly pure ethoxyacetonitrile, $NC—CH_2.OC_2H_5$.

The nitril is a colourless liquid, having a peculiar but not unpleasant odour; it is very slightly soluble in water, but readily so in alcohol and ether. Its boiling point is 132—133°, and its density 0·9093 at 20°. Alcoholic potash decomposes it, with formation of ammonia, while nascent hydrogen produces a small quantity of a base which is probably the ethylated derivative of hydrox-ethylenamine. Details are given in the paper respecting the formation of ethyl-glycollic ether and its corresponding amide. J. W.

On Monochlorethyl-acetamide. By T. H. NORTON and J. TCHERNIAK (*Compt. rend.*, lxxxvi, 1409—1411).—One of the authors has proved that dichlorethylamine contains two chlorine-atoms directly united to the nitrogen atom, since on treatment with zinc-ethyl it yields triethylamine. The present research was undertaken for the purpose of preparing a *mono*chlorinated body of a similar constitution. With this object the halogens were allowed to act upon ethyl-acetamide. The action of chlorine was very violent, but if the liquid was surrounded with a freezing-mixture, the action could be arrested when, by the increase of weight, one molecule of chlorine was known to have been absorbed. No hydrochloric acid was evolved, but on removing this acid from the product by adding potassium carbonate to the ice-cold solution in water, a colourless oily layer floated on the surface. This proved to be the monochlorethyl-acetamide mixed with ethyl-acetamide, and even by special treatment the mixture could not be obtained with less than 10 per cent. of the latter. An analogous bromo-substitution-product was obtained by warming ethyl-acetamide with a solution of bromine in potassium bromide; the product, treated with aqueous solution of potassium carbonate, yields a heavy oil, which is a mixture of monobromethyl-acetamide with ethyl-acetamide. Both these halogen derivatives are neutral liquids, soluble in water, alcohol, and ether, undergoing decomposition rapidly when distilled, and more slowly on standing. Boiling soda-solution decomposes the chloro-derivative into chloroform, dichlorethylamine, ethylcarbylamine, and ethylamine. F. C.

Action of Bromine in Presence of Aluminium Bromide on the Homologues of Benzene. By G. GUSTAVSON (*Bull. Soc. Chim.* [2], xxx, 22).—Some of the homologues of benzene when subjected to the action of bromine in presence of aluminium bromide, are simply converted into bromo-derivatives, while others are decomposed, with separation of radicles of the fatty series.

Isopropylbenzene treated in the above way is decomposed, with formation of hexbromobenzene and separation of isopropyl, which, by the action of bromine is converted into brominated compounds boiling between 100° and 220°.

Cymene in the same circumstances gives only monobromisopropyl, which the author attributes to the difference in the rate of bromination in the two cases.

Isobutylbenzene behaves like isopropylbenzene, while *ethylbenzene* produces pentabromethylbenzene. The author therefore concludes that ethyl and methyl are not separated by this treatment, whilst the radicles propyl and butyl, and probably also the more complex radicles, are separated. C. W. W.

Cymene and Cymyl Alcohol. By K. KRAUT (*Liebig's Annalen*, cxcii, 222—227).—Cymene, prepared by the action of zinc-dust on cymyl alcohol, boils at 174·8°, has a specific gravity of 0·8732 at 0°, and is identical with the cymene obtained directly from cumin oil.

W. C. W.

Oxidation of Nitrogenous Compounds by Potassium Permanganate. II. By S. HOOGEWERFF and W. A. VAN DORP (*Deut. Chem. Ges. Ber.*, xi, 1202—1206).—*Aniline.*—As previously shown (p. 297 of this volume), aniline on oxidation by potassium permanganate, yields oxalic acid, azobenzene, and ammonia. About 23 per cent. of the carbon of the aniline is converted by this means into oxalic acid.

Orthotoluidine (b. p. 197°), on oxidation in the same manner as that described for aniline, gave ammonia, orthoazotoluene, and oxalic acid in the following proportions:—About 49 per cent. of the nitrogen of the toluidine was converted into ammonia; about 30 per cent. of the quantity of azotoluene which could theoretically be obtained from toluidine; about 24 per cent. of the quantity of oxalic acid which could be got theoretically, neglecting the methyl-group, or 1 molecule of the base yields 3 molecules of oxalic acid.

The orthoazotoluene obtained in this way crystallised from ether in red prisms (m. p. 55°). It is easily soluble in alcohol, ether, benzene, carbon bisulphide, and chloroform, but is insoluble in water. It is readily volatile in steam, and is not attacked by boiling sodic hydrate solution. It dissolves in sulphuric acid, from which it is precipitated unchanged on addition of water. Barsylowsky (*Ber.*, x, 2097) gives 137° as the melting point of orthoazotoluene; his meta-azotoluene, however, resembled the author's ortho-compound both in its melting point and its other properties.

Paratoluidine gives results similar to orthotoluidine, both as to the quantity and nature of the bodies produced, except that para-azotoluene is obtained in place of the ortho-compound, and that only about 40 per cent. of the nitrogen in paratoluidine is converted into ammonia, while about 49 per cent. of the nitrogen was converted into ammonia in the case of orthotoluidine. The authors are unable to account for this difference.

By careful oxidation, nitrates and nitrites are produced in far less quantity (1—2 per cent.) in these reactions than was formerly supposed to be the case, whilst the quantity of carbonic acid is greater.

There is also obtained, in addition to the substances above mentioned, a small quantity of a black nitrogenous body, and a nitrogenous acid; this has not been further investigated. T. C.

Nitration-products of Symmetric Dichloraniline. By BEILSTEIN and KURBATOFF (*Bull. Soc. Chim.* [2], xxx, 25).—By the nitration of symmetric dichloraniline, two dichloronitranilines are produced, one melting at 170—171°, and forming an acetyl-derivative melting at 222°; whereas the other melts at 79°, and its acetyl-derivative at 138—139°.

The first body, treated with nitrous ether, gives a compound, $C_6H_3Cl_2(NO_2)$ (m. p. 71°), which changes into dichloraniline (m. p. 39°), and forms an acetyl-derivative (m. p. 175°); the second dichloronitraniline gives with nitrous ether, metachloronitrobenzene (m. p. 33°). C. W. W.

Action of Halogen Sulphur-compounds on Aniline, Acetanilide, and Benzene. By E. B. SCHMIDT (*Deut. Chem. Ges. Ber.*, xi, 1168—1175).—*Iodide of Sulphur and Aniline.*—As previously shown (*Ber.*, ix, 1050), the action of iodide of sulphur on aniline at 160—170° results in the formation of thioaniline (m. p. 105°), and a considerable quantity of a dark resinous body, probably containing dithioaniline.

Bromide of Sulphur and Aniline.—Bromide of sulphur acts so violently on aniline, even when the mixture is well cooled, that it is necessary to dilute very largely with benzene. A considerable quantity of a highly sulphuretted resinous mass is thus obtained, which dissolves in benzene, and remains after distilling off the latter. From the residue a small quantity of dithioaniline, $(C_6H_3NH_2)_2S_2$, may be extracted by strong hydrochloric acid, and subsequent precipitation by much water and afterwards ammonia. Thioaniline is also produced simultaneously with the dithioaniline; no evolution of sulphuretted hydrogen or separation of sulphur occurs during the reaction.

Chloride of Sulphur and Aniline by a similar process likewise give thioaniline and a resinous mass, which probably consists chiefly of dithioaniline.

Acetanilide and Chloride of Sulphur.—Chloride of sulphur acts on acetanilide only at 100°, with evolution of hydrochloric and a little acetic acid. From the dark brown brittle mass obtained, glacial acetic acid dissolves two bodies, the least soluble of which is trithioacetanilide, and the other dithioacetanilide.

Trithioacetanilide, $(C_6H_4NH.C_2H_3O)_2S_3$, crystallises from glacial acetic acid in small pearly plates (m.p. 214°), which in time assume a yellowish colour. Of the usual solvents, alcohol is the only one in which it dissolves, and that more readily when hot than when cold. By long heating with sulphuric or hydrochloric acid, it is decomposed, like acetanilide, into acetic acid and the corresponding sulphur base; the latter, being of a resinous character, has not been investigated.

Dithioacetanilide, $(C_6H_4NH.C_2H_3O)_2S_2$, crystallises from glacial acetic acid in greyish-white plates (m. p. 216°). It is soluble in alcohol, from which it separates out, after long exposure to the air, in sharp pointed needles. It is but little, if at all soluble in other solvents, and is decomposed by acids into acetic acid and pseudo-dithioaniline. This base gives a stable and characteristic sulphate.

Dithioaniline sulphate, $C_{12}H_{12}N_2S_2.H_2SO_4 + 2H_2O$, consists either of a network of radiating needles, or nodular masses, which are white when freshly prepared, but gradually become red on exposure. The salt loses its water of crystallisation at 110—120°. The hydrochloride is a very unstable salt, being decomposed even on exposure to the air.

Pseudo-dithioaniline, $C_{12}H_{12}N_2S_2$, is a stable and well-marked compound, which can be obtained from the hot aqueous solution of its salts by addition of alkali. It crystallises from a large quantity of hot water in brilliant greenish needles (m. p. 78°), and is easily soluble in alcohol and still more easily in ether and chloroform; it is but little soluble in cold benzene, petroleum ether, or carbon bisulphide, but more readily when hot. This thioanilide differs from that prepared by the action of sulphur bromide on aniline, for the latter can only be obtained as a resin, whilst the pseudo-dithioaniline is a well-crystallised body. They also differ in their unequal solubility in hydrochloric acid. The author explains the constitution of these bodies as follows:—

Pseudo-dithioaniline, $NH_2.C_6H_4—S—S—C_6H_4.NH_2$.

Dithioaniline, $NH_2.C_6H_3{<}\substack{S\\S}{>}C_6H_3.NH_2$.

Chloride of Sulphur and Benzene.—These two bodies react on one another only at 250° in sealed tubes, when monochlorbenzene is obtained, whilst hydrochloric acid is evolved and monoclinic sulphur is deposited, thus:—

$$C_6H_6 + S_2Cl_2 = HCl + C_6H_5Cl + S_2.$$

No sulphobenzene derivatives are produced.

Chloride of Sulphur and Benzene in presence of Zinc.—When zinc-dust is added to a hot mixture of sulphur chloride and benzene, a very violent action occurs, hydrochloric acid, but no sulphuretted hydrogen, being evolved. From the resulting mass benzene extracts a clear, dark red-brown liquid, from which a small quantity of phenyl-disulphide (m. p. 60°) may be obtained by distillation with steam and recrystallisation from alcohol. Another portion of the viscous mass, when distilled alone, was completely decomposed, with evolution of hydrochloric acid, and then sulphuretted hydrogen in increasing quantity, and final charring of the residue. The distillate was found to contain phenyl-sulphydrate, $C_6H_5.SH$ (b. p. 168·5°), phenyl-monosulphide, $(C_6H_5)_2S$ (b. p. 293°), and diphenyl-disulphide, $(C_6H_4)_2S_2$ (m. p. 156°), already described by Graebe (*Ber.*, vii, 51).

By the above reaction of chloride of sulphur and benzene in presence of zinc, an organic zinc-compound containing sulphur was also produced, but could not be obtained in the pure state. T. C.

Ortho-dinitro-Compounds. By A. Laubenheimer (*Deut. Chem. Ges. Ber.*, xi, 1155—1161).—Orthonitraniline (m. p. 71·5°), together with ammonium nitrite, is produced by the action of alcoholic ammonia on ortho-dinitrobenzene at 100—110°. Thus: $C_6H_4(NO_2.)(NO_2.) + 2NH_3 = C_6H_4(NO_2)(NH_2) + NH_4.NO_2$.

Nitro-chlorophenyl-ethylamine, $C_6H_3(ClNO_2)(NH.C_2H_5)$, is obtained when dinitro-chlorbenzene, $C_6H_3(ClNO_2)(NO_2)$, is shaken up with an alcoholic solution of ethylamine. It crystallises in gold-yellow needles (m. p. 83°), which dissolve with difficulty in cold alcohol, but easily in hot alcohol and in ether. It is almost insoluble in water, dilute hydrochloric, nitric or sulphuric acids, but more soluble in acetic and fuming hydrochloric acids.

Nitrochlorophenyl-paratolylamine, $C_6H_{13}(ClNO_2)(NH.C_7H_7)$.—When 1 mol. dinitrochlorbenzene and 3 mols. paratoluidine, made up to a paste with alcohol, are allowed to stand at the ordinary temperature for 24 hours, a solid crystalline mass is obtained, consisting of red and yellow crystals. The red crystals are the above compound, and the yellow consist of diazoamido-toluene, $C_7H_7.N{=}N.NH(C_7H_7)$. The former is obtained pure by warming the mass with glacial acetic acid, whereby the diazo-compound is decomposed into cresol and toluidine, which are easily removed by their greater solubility in the acetic acid.

Nitrochlorophenyl-tolylamine crystallises in small red needles (m. p. 124°), which dissolve with difficulty in cold alcohol, but are easily soluble in hot alcohol and in glacial acetic acid.

Nitrochlorophenyl-metaphenylenediamine,

$$C_6H_3Cl(NO_2).NH.C_6H_4.NH_2,$$

is obtained by gently warming a mixture of equal parts of metaphenylenediamine and dinitrochlorobenzene with alcohol until solution is complete, and allowing the whole to stand at the ordinary temperature for two days. The product is afterwards extracted with cold hydrochloric acid, and the resulting hydrochloride decomposed into free base and acid by solution in hot alcohol; the base is then obtained pure by recrystallisation from alcohol. It crystallises in carmine-red silky needles (m. p. 150°), and dissolves with difficulty in cold alcohol, but easily in hot alcohol and in ether; it is almost insoluble in water, and unites with acids to form unstable yellow salts.

Attempts to prepare a definite compound with naphthylamine and dinitrochlorbenzene were unsuccessful.

Dinitrochlorbenzene has no action on urea in the cold, but, after several hours' heating at 165°, nitrochloraniline, $C_6H_3(NH_2)(NO_2)Cl = (1:2:5)$, is obtained (m. p. 123°). Acetanilide behaves in a manner similar to urea. Thus:—

$$C_6H_3Cl(NO_2)_2 + 2(C_2H_3O.NH_2) = C_6H_3Cl(NO_2)(NH_2) + 2C_2H_4O_2 + N_2.$$

Nitrobromophenol, $C_6H_3(OH)(NO_2)Br = (1:2:5)$.—When dinitrobrombenzene, $C_6H_5Br(NO_2)NO_2$ (1 : 3 : 4 :) (obtained by nitrating metanitrobrombenzene), is boiled with aqueous potash (sp. gr. 1·135), and the liquid afterwards acidified with sulphuric acid and distilled, two nitrobromophenols pass over with the distillate. These may be separated by crystallisation from petroleum. The one occurring in smallest quantity consists of $C_6H_8(OH)(NO_2)Br = (1:2:4)$ (m. p. 88°), and is identical with the nitrobromphenol obtained by Brunck

(*Zeit. f. Chem.* [1867], 202); that occurring in largest quantity is $C_6H_3(OH)(NO_2)Br = (1:2:5)$, crystallising in prisms (m. p. 44°). It is easily soluble in alcohol, ether, and petroleum, and volatile in steam.

Sodium salt, $C_6H_3(BrNO_2).ONa$. Scarlet needles, easily soluble in water.

Barium salt $(C_6H_3BrNO_2.O)_2Ba + H_2O$. Crystallises in dark red needles, very difficultly soluble in water.

The calcium and silver salts were also prepared. T. C.

Constitution of Benzene Derivatives. By E. WROBLEWSKY (*Liebig's Annalen*, cxcii, 196—221).—The author has shown on a former occasion (*Annalen*, clxviii, 147) that on brominating acetoparatoluide, the bromine occupies the meta position, forming *acetometabromo-paratoluide* (m. p. 117·5°). From this compound he obtained metabromotoluene (1 : 3), which yields metabromobenzoic acid on oxidation, and from which meta-ethyltoluene can be prepared by the action of sodium and ethyl bromide. On oxidation, meta-ethyltoluene is converted into isophthalic acid.

Acetometabromotoluide yields a nitro-compound,

$$C_6H(CH_3)Br(NO_2).NH.C_2H_3O$$

(m. p. 210·5°), crystallising from an alcoholic or acetic acid solution in white needles. By the action of soda-solution, this body is changed into *bromonitrotoluidine*, $C_6H_2(CH_3)Br(NO_2)NH_2$ (1 : 3 : 5 : 4), which crystallises in orange-coloured needles (m. p. 64·5).

α-Bromonitrotoluene, $C_6H_3(CH)Br.NO_2$ (1 : 3 : 5), prepared from bromonitrotoluidine, melts at 86°, and boils at 269—270°; on reduction with tin and hydrochloric acid, it yields *bromotoluidine*, $C_6H_3(CH_3)Br.NH_2$ (1 : 3 : 5). This base boils at 255—260°; it does not solidify at −20°; its sp. gr. at 19° is 1·1442. It forms a series of well-crystallised salts, *e.g.*, $C_7H_6Br(NH_2).HCl$, colourless plates, which sublime readily.

$C_7H_6Br.NH_2.HNO_3$. Long pink needles; 24·9 parts of the nitrate dissolve in 1000 parts of water at 13°.

$(C_7H_6Br.NH_2)_2H_2SO_4$ forms colourless plates. Sodium amalgam slowly converts bromotoluidine into metatoluidine (b. p. 197°), $C_6H(CH_3)NH_2$ (1 : 5), from which metabromotoluene, $C_6H_4(CH_3)Br$ (1 : 5) (b. p. 182°), and metabromobenzoic acid (m. p. 154°), were prepared. The author concludes from these experiments that the bromotoluenes 1 : 3 and 1 : 5 are identical.

A mixture of ortho- and para-toluidine may be used for preparing *bromonitrotoluene* 1 : 3 : 5 (m. p. 86°), since on brominating orthotoluidine, the bromine occupies the meta position. *Bromonitro-orthotoluidine*, $C_6H_2(CH_3)Br(NO_2).NH_2$ (1 : 3 : 5 : 6), crystallises in orange-coloured prisms, which melt at 139°; it is converted by Griess's reaction into bromonitrotoluene (1 : 3 : 5).

To prove that the derivatives 1 : 2 and 1 : 6 are identical, the author started from *dibromiodotoluene*, $C_6H_2(CH_3)BrIBr$ (1 : 3 : 4 : 5), which he prepared (I) from metabromo-metanitro-paratoluidine, $C_6H_2(CH_3)Br(NH_2)NO_2$ (1 : 3 : 4 : 5), by replacing the NH_2-group by iodine, reducing the nitro-group to NH_2, and replacing the latter by bromine; or (II) more easily by substituting iodine for NH_2 in dibromo-paratoluidine, $C_6H_2(CH_3)Br(NH_2)Br$ (1 : 3 : 4 : 5), (*Annalen*, clxviii, 147). Dibromiodotoluene crystallises in long needles (m. p. 86°, b. p. 270°); by the action of nitric acid, sp. gr. 1·43, it is converted into nitro-dibromiodo-toluene, $C_6H(CH_3)(NO_2)BrIBr$ (1 : 2 : 3 : 4 : 5), which forms large needles (m. p. 69°). On reduction with tin and hydrochloric acid, dibromoiodotoluidine (m. p. 64°) is formed. This base is slowly reduced by sodium amalgam to orthotoluidine (1 : 2).

But orthotoluidine can also be obtained from *dibromiodotoluidine*, $C_6H(CH_3)(NH_2)BrIBr$ (1 : 2 : 3 : 4 : 5): for by decomposing the diazo-compound of this body with hydriodic acid, dibromo-diiodotoluene, $C_6H(CH_3)IBrIBr$ (1 : 2 : 3 : 4 : 5) is formed. By the action of tin and hydrochloric acid, the nitro-derivative, $C_6(CH_3)(IBrIBr)NO_2$ (1 : 2 : 3 : 4 : 5 : 6) is converted into an amido-compound, which yields orthotoluidine (1 : 6) on reduction with sodium amalgam.

Bromoxylene, prepared by the action of nitrous acid on an alcoholic solution of bromoxylidine, is a colourless liquid; sp. gr. 1·362 at 20°, boiling at 204°. Dimethylethylbenzene is formed by treating a mixture of bromoxylene, ether, and ethyl bromide with sodium; it is a colourless liquid, boiling at 185°, sp. gr. 0·861 at 20°. It yields uvitic and mesitylenic acids on oxidation.

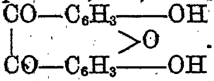
Ortho-, meta-, and para-dibromobenzene, when heated with bromine and water in sealed tubes at 250°, all yield the same tribromobenzene (1 : 3 : 4) (m. p. 44°). W. C. W.

Metachlorophenol. By E. UHLEMANN (*Deut. Chem. Ges. Ber.*, xi, 1161—1162).—The author finds that this body may be prepared much more readily than in the ordinary way (*i.e.*, from meta-chloraniline by the diazo-reaction) by the action of nitrous acid on finely powdered metachloraniline nitrate, suspended in water and well cooled, until all has dissolved. A cold strong solution of mercuric chloride is then added, which produces a precipitate of a double mercury salt; this is very difficultly soluble in cold, but much more easily in warm water. The aqueous solution of this salt is heated until nitrogen ceases to be evolved, sodic hydrate is then added, and the solution filtered from the oxide of mercury thrown down; the meta-chlorophenol is finally extracted from the acidified filtrate by ether. The pure compound boils at 211° (corr.) and melts at 28·5°.

Nitro-chlorophenol, $C_6H_3(OH)Cl(NO_2)$ = (1 : 3 : 6), identical with that described by Laubenheimer (*Ber.*, xi, 768), is obtained by adding meta-chlorophenol to well-cooled nitric acid (sp. gr. 1·42), or better by the action of nitrous acid on the aqueous solution of meta-chloraniline nitrate. It forms lemon-yellow prisms or needles, and exhibits the characteristic double melting points, 38·9° and 32·7°.

Nitrochlorophenol methyl ether, $C_6H_3Cl(NO_2)OCH_3$, is prepared from the silver salt and methyl iodide; it crystallises from alcohol in long flat yellowish-green needles (m. p. 70·5), which are easily soluble in ether and hot alcohol. On heating with alcoholic ammonia at 180° for 10 hours, it yields nitrochloraniline, $C_6H_3(NH_2)Cl.NO_2$ = (1 : 3 : 6) (m. p. 123·5°). T. C.

Action of Oxalic Acid on Resorcin. By P. GUKASSIANZ (*Deut. Chem. Ges. Ber.*, xi, 1148—1187).—This is an attempt to prepare a resorcin-aurin by the action of oxalic and sulphuric acids on resorcin, in a manner analogous to that by which aurin is obtained from phenol. Thus: $(CO.OH)_2 + 2C_6H_4(OH)_2 = [CO.C_6H_3(OH)_2]_2 + 2H_2O$. (*see* p. 980). For this purpose 2 molecules of resorcin and 1 molecule of oxalic acid were heated with strong sulphuric acid (or glycerin or phosphorus pentoxide) at 120°, when a somewhat violent reaction occurred; the mass, after 4 or 5 hours, became solid. The nature and proportions of the gases evolved were determined, and were found to consist of equal volumes of carbon monoxide and carbon dioxide; they are produced, as in the case of the formation of aurin, by the decomposition of a portion of the oxalic by the sulphuric acid, the rest of the oxalic acid entering into double decomposition with the resorcin. The dark-brown solid mass obtained by the reaction was boiled with water until free from sulphur acids, and then dissolved in potash solution. This solution had a dark brownish-red colour, and, on considerable dilution, exhibited a moss-green fluorescence. The author was unable to obtain the substance in a crystalline form, but he found that it could be separated into two portions, one soluble and the other insoluble in alcohol. The insoluble bright yellow amorphous portion dissolved easily in potassic hydrate, yielding a green fluorescent liquid; the portion soluble in alcohol, on the contrary, was a dark-brown mass, which, although easily soluble in potassic hydrate, gave not a yellowish-red but a brown liquid, which was not in the least fluorescent. Analysis showed that both these bodies had the same composition, viz., $C_{14}H_{10}O_6$, or were anhydrides of resorcin-aurin; thus:—



$$\begin{array}{l} CO—C_6H_3——OH \\ | \qquad >O \\ CO—C_6H_3——OH \end{array}$$

. Both substances were exceedingly hygroscopic and could be obtained dry only at 130—135°; they gave characteristic bromo- and nitro-compounds, which have not yet been studied.

T. C.

Formation of Aurin. By P. GUKASSIANZ (*Deut. Chem. Ges. Ber.*, xi, 1179—1184).—Baeyer (*Ber.*, iv, 660) has explained the formation of aurin from phenol, oxalic and sulphuric acids, as being due to the combination of the carbonic acid set free from the oxalic acid with either 2 or 4 molecules of phenol, and liberation of 1 or 2 molecules of water respectively. Kolbe (*Jour. f. pr. Chem.*, cxiii, 204), on the other hand, believes that it consists in a simple addition of the nascent carbon monoxide, set free by the decomposition of the oxalic acid, to 1 molecule of phenol; thus: $C_6H_5.OH + CO = C_6H_4.O.CH(OH)$; whilst Dale and Schorlemmer (*Annalen*, clxvi, 292) represent the formation of aurin as follows: $3C_6H_6O + 2CO = C_{20}H_{14}O_3 + 2H_2O$. The assumption in the last two cases, viz., that it is the carbonic oxide which is the reacting body, is based on the experiments of H. Fresenius (*Jour. f. pr. Chem.*, v, 193) and also of Erhart (*Arch. f. Pharm.*, ccxi, 500), according to whom the gases evolved in the reaction consist chiefly of carbonic acid. The former chemist also obtained aurin from phenol, on substituting formic acid or potassium ferrocyanide for oxalic acid.

The author finds that none of the above explanations are correct, and that neither the carbon monoxide nor dioxide is the necessary agent in the formation of aurin, but that the oxalic acid, as such, combines with 2 molecules of phenol, with liberation of 2 molecules of water. If this be true, the formation of aurin is exactly analogous to that of phthaleïn; thus:—

$$C_6H_4(COOH)_2 + 2C_6H_5(OH) = C_6H_4(CO.C_6H_4.OH)_2 + 2H_2O$$
$$(COOH)_2 + 2C_6H_5(OH) = (CO.C_6H_4.OH)_2 + 2H_2O.$$

In confirmation of this view, experiments are detailed which show that Fresenius and Erhart's statement with regard to the gases evolved during the reaction is incorrect, for the carbon monoxide and carbon dioxide (which are obtained in equal volumes) are due to the decomposition by the sulphuric acid of those portions of the oxalic acid which do not enter into combination with the phenol; while another portion of oxalic acid, as such, enters into double decomposition with the phenol to form aurin.

The author has likewise repeated Fresenius's experiments as to the preparation of aurin by the use of formic acid or potassium ferrocyanide in place of oxalic acid, but has been unable to obtain aurin in either case, only a small quantity of a resinous body quite different from aurin being formed.

From a number of analyses, the formula $C_{14}H_{10}O_4$ is assigned to aurin. Aurin was best obtained pure by dissolving the crude substance in hot dilute sulphuric acid, from which, on cooling, crystals were deposited; these, after washing with water, were dissolved in sodic hydrate, and the aurin precipitated by hydrochloric acid, and afterwards washed until free from hydrochloric and sulphuric acids.

T. C.

The Lemon-yellow Nitro-benzoic Acid. By F. FITTICA (*Deut. Chem. Ges. Ber.*, xi, 1207—1210).—The lemon yellow nitrobenzoic acid (m. p. 142°) was converted into the amido-acid, and the latter into the sulphate of the corresponding diazo-benzoic acid by passing nitrous acid into a mixture of the amido-acid and dilute sulphuric acid (1 part acid to 3 of water). The *sulphate of the diazobenzoic acid* thus obtained crystallises in pale yellow needles, which are easily soluble in water, but insoluble in alcohol and ether. By decomposition with water, according to Griess's reaction, it gives an *oxybenzoic acid*, $C_6H_4(OH).COOH$, which is isomeric and not identical with the three known oxybenzoic acids.

New Oxybenzoic acid.—This acid melts at 190°, whilst that from meta-amidobenzoic acid melts at 201°. It is likewise distinguished from the latter by its greater solubility in water; for 1 part of the new acid dissolves in 45·8 parts of water at 18°, whilst 1 part of the meta-oxybenzoic acid dissolves in only 108·2 parts of water at the same temperature; nor is the new acid volatile with steam.

The barium salt $[C_6H_4(OH).COO]_2Ba + H_2O$, retains 1 molecule of water even at 100°. It could only be obtained in an amorphous state, in which respect it differs from the barium salt of meta-oxybenzoic acid. Both salts are very easily soluble in cold water, and that of the new acid also in alcohol; the latter acid appears to form a liquid ethyl salt; metaoxybenzoic acid does not.

By decomposition with alcohol, the sulphate of the diazobenzoic acid, corresponding with the yellow nitrobenzoic acid (m. p. 142°), is remarkable in giving ethyloxybenzoic acid, $C_6H_4(OC_2H_5).COOH$, which, from its m. p. 138° and great solubility in water, appears to be identical with that described by Heintz (*Annalen*, cliii, 334). It differs from the latter, however, in that the barium salt of Heintz's acid crystallises from water with 1 molecule of water, and is less soluble in cold than in hot water; whilst the barium salt of the new acid is just as soluble in hot as in cold water, and does not crystallise from the latter; from alcohol it separates in nodular anhydrous crystals. By decomposition with alcohol, the sulphate of the new diazobenzoic acid, unlike that of the diazo-compound from meta-nitrobenzoic acid, gives benzoic acid, and not ethyl-oxybenzoic acid. The yellow nitro-benzoic acid of m. p. 135°, as well as that of m. p. 128°, yields the same diazo-compound as the acid of m. p. 142°. T. C.

Preliminary Notice on Phenylglyceric Acid and Related Compounds. By R. ANSCHÜTZ and L. KINNICUTT (*Deut. Chem. Ges. Ber.*, xi, 1219—1221).—*Methyl cinnamate*,

$$C_6H_5.CH{=}CH.COOCH_3,$$

is a white solid body, having a very pleasant odour; it is easily soluble in all the ordinary solvents except water. It melts at 33·4° and boils at 263°. Kopp (*Annalen*, lx, 269), however, describes it as a liquid boiling at 241°.

Ethyl cinnamate, $C_6H_5.CH{=}CH.COOC_2H_5$, is a colourless liquid of pleasant odour (b. p. 271°, Kopp, 263°).

Normal propyl cinnamate, $C_6H_5.CH{=}CH.COOC_3H_7$, is also a colourless liquid (b. p. 283).

Methyl-phenyl Dibromopropionate, $C_6H_5.CHBr.CHBr.COOCH_3$, separates in the crystalline state on the addition of bromine to the ethereal solution of methyl cinnamate. It crystallises from ether in colourless transparent crystals (m. p. 117°), soluble in all the ordinary solvents except water.

Ethyl-phenyl Dibromopropionate, $C_6H_5.CHBr.CHBr.COOC_2H_5$, is obtained like the methyl ether. It is easily soluble in all solvents except water, and separates from its solution in ether or chloroform in large colourless crystals (m. p. 69°). It is not decomposed by boiling with water.

Ethyl Dibenzoylphenylglycerate,

$$C_6H_5.CH(OC_6H_5CO).CH(O.C_6H_5CO).COOC_2H_5,$$

is obtained on boiling a solution of ethyl-phenyl dibromopropionate in toluene with somewhat more than the calculated quantity of silver benzoate for three days, and can be separated from the benzoic acid simultaneously produced by crystallisation from alcohol, in which it is but little soluble. It forms striated crystals which melt at 109°.

T. C.

Substances obtained from Strawberry Roots. By T. L. PHIPSON (*Chem. News*, xxxviii, 135).—Strawberry root contains a kind of tannin called *fragarianin*, having a pale-yellow colour, soluble in water, alcohol, and slightly acidulated water, and giving a green colour with ferric salts. It forms an insoluble compound with hydrochloric acid, and is precipitated in purple flakes by alkalis. Fragarianin may be obtained pure by evaporating an aqueous solution in an atmosphere of carbon dioxide; when boiled with dilute acids it yields *fragarin*, which may be obtained from the root by digesting 5 grams with a 5 per cent. hydrochloric acid solution for 48 hours, when the solution is filtered, strongly acidified, and boiled. As the temperature rises the colour changes from yellow to orange, and, after boiling for some time, fragarin separates out as a reddish-brown amorphous powder, soluble in water, alcohol, and ether, and dissolving in potash with a reddish-purple colour. It forms a compound with sulphuric acid, and a yellow nitro-compound when treated with nitric acid. When heated with hydrochloric acid and potassium chlorate, it yields a yellow chlorine compound insoluble in water and decomposed by ammonia. It chars when heated, probably yielding protocatechuic acid, which is also formed when fragarin is fused with potash. Cinchona-red and fragarin may be distinguished by their action with caustic potash, the former giving a dirty-green colour and the latter a reddish-brown solution.

Strawberry root also contains a body similar to quinovin, which yields a substance resembling, but not identical with, quinovic acid. It also contains a small quantity of gallotannic acid. L. T. O'S.

Neutral Ethyl Salt of Nitrophthalic Acid, and Baeyer's Oxyphthalic Acid. By O. Miller (*Deut. Chem. Ges. Ber.*, xi, 1191—1193).—The author corrects his former statement (*Ber.*, xi, 962) that ethyl isonitrophthalate can be readily crystallised whilst ordinary nitrophthalate can be obtained only as a non-crystallisable oil; for he now finds that the pure ethyl salt of ordinary nitrophthalic acid cannot be prepared by the action of hydrochloric acid gas on the alcoholic solution of the acid, as a portion of the nitro-acid is reduced to phthalic acid, and the ethyl compound previously supposed to be pure was therefore a mixture of the nitrophthalate and phthalate. The pure ethyl salt of ordinary nitrophthalic acid can, however, be readily obtained by the action of ethyl iodide on the silver salt. It is a colourless crystalline substance, m. p. 43°.

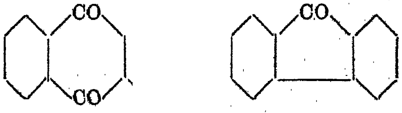
The oxyphthalic acid of Baeyer (*Ber.*, x, 1083) does not correspond with ordinary, but with iso-nitrophthalic acid. For as the ordinary nitro-acid, from which he prepared his oxy-acid, was obtained by Faust's method (*Annalen*, clx, 56), it could not be pure, but would contain in addition an almost equal quantity of isonitrophthalic acid, as the author has previously shown (*loc. cit.*); and further, as Baeyer's method of preparing the oxy-acid from the nitro-acid was such as to convert the iso- and not the ordinary nitro-acid into oxy-acid, the oxy-acid he obtained would correspond, not with the ordinary, but with iso-nitrophthalic acid. The author has proved the truth of this by submitting pure iso-nitrophthalic acid to the treatment described by Baeyer for obtaining the oxyphthalic acid, and has by this means obtained an oxy-acid identical with that prepared by Baeyer. In the course of this last experiment he found that the ethyl amido-phthalate, obtained by reduction from the acid ether of iso-nitrophthalic acid (m. p. 32°), crystallises in large short prisms (m. p. 95°).

Iso-oxyphthalic acid crystallises from ether in dirty-coloured microscopic tables melting at 180°, and at the same time undergoes conversion into the anhydride (m. p. 165°). The aqueous solution of the acid is coloured reddish-yellow by ferric chloride. T. C.

Chloronaphthylamine. By P. SEIDLER (*Deut. Chem. Ges. Ber.*, xi, 1201—1202).—This compound is obtained when a mixture of naphthylamine and stannous chloride is exposed to the air for several weeks. It can be separated from unchanged naphthylamine by fractional crystallisation from benzene, in which it is but little soluble. It is readily soluble in alcohol and ether, and crystallises in colourless needles (m. p. 98°). It possesses basic properties, uniting with acids to form crystalline salts.

Acetyl-chloronaphthylamine, $C_{10}H_6Cl.NH(C_2H_3O)$, is obtained by long boiling of chloronaphthylamine with glacial acetic acid, and recrystallisation from this latter solvent. It crystallises in colourless needles (m. p. 184°), easily soluble in alcohol and ether. T. C.

Diphenylene Ketone from Anthraquinone and Pyrocondensation-products. By R. ANSCHÜTZ (*Deut. Chem. Ges. Ber.*, xi, 1213—1216).—Anthraquinone, when heated with 20 times its weight of caustic lime, yields diphenylene ketone together with small quantities of diphenyl, anthracene, and fluorene. This reaction seems to indicate that the CO-groups in anthracene occupy the diortho-position, thus:—



Anthraquinone. Diphenylene ketone.

for Anschütz and Japp (*Ber.*, xi, 211) have shown that diphenylene ketone on oxidation gives phthalic acid, and therefore that in diphenylene ketone the CO-group is in the diortho-position.

On the other hand, the fact that all the members of Græbe's diphenylene-series have the substituting atoms or atom-groups in the diortho-position with reference to the points of combination of the benzene neuclei, and also that all these diphenylene compounds can be formed by condensation pyro-reactions from the corresponding diphenyl compounds, is not easily reconciled with the above theory of the constitution of anthraquinone.

The author proposes the following law, by the help of which he endeavours to explain why fluorene and phenanthrene occur in such large quantities in the high-boiling portions of coal-tar:—Pyro-condensations from phenyl-phenyl derivatives to phenylene-phenylene derivatives always take place in such a way that the atoms or atom-groups connecting the phenylene nuclei, assume the diortho-position with reference to the points of combination of the phenylene nuclei. T. C.

Monobromophenanthrene and Phenanthrene Dibromide. By R. Anschütz (*Deut. Chem. Ges. Ber.*, xi, 1217—1219).—The author, like Hayduck (*Annalen*, clxvii, 181), has been unable to convert monobromophenanthrene into the tolane corresponding with phenanthrene, even by long-continued heating at 170° with the most concentrated potash solution. The bromine-atom in monobromophenanthrene is probably in the same position as the oxygen-atoms in phenanthrenequinone, for on oxidation it yields the latter substance. Its constitution is therefore $(C_6H_4)_2.C_2HBr$; it can be sublimed without decomposition, and is not decomposed by distillation at a temperature above 360°.

When monobromophenanthrene, dissolved in glacial acetic acid, is warmed with nitric acid, a mixture of at least two nitro-compounds is precipitated on the addition of water, in the form of yellow microscopic needles. From this mixture, carbon bisulphide or ether extracts one of the bodies, and leaves the other as a reddish-yellow substance, which has not been further examined. The soluble portion after recrystallisation yields fine prisms or compact crystals (m. p. 195°), which sublime in long needles. Analysis showed that this substance is *mononitrobromophenanthrene*, $C_{12}H_7(NO_2).C_2HBr$.

Phenanthrene dibromide appears to give a nitro-product when treated with nitric acid, in acetic acid solution. An alcoholic solution of phenanthrene dibromide, when acted on by potassium cyanide, yields phenanthrene. Stilbene bromide, in a similar manner, gives stilbene. This reaction is parallel to that which occurs when diphenyl-succinic acid is obtained from ethyl monobromophenylacetate by means of potassium cyanide (*Bull. Soc. Chim.*, xix, 106), the one being an extra- and the other an intra-molecular condensation. T. C.

Anthrarufin, a New Dioxyanthraquinone from Metaoxybenzoic Acid. By E. Schunck and H. Römer (*Deut. Chem. Ges. Ber.*, xi, 1176—1179).—By the action of strong sulphuric acid on metaoxybenzoic acid two products are obtained, one of which is soluble in water, and the other insoluble. The latter is again divisible into two parts, one soluble in baryta-water and consisting of the two dioxyanthraquinones, anthraflavic acid, and metabenzodioxyanthraquinone (*Ber.*, xi, 969), and the other insoluble, consisting of a third dioxyanthraquinone, to which the name anthrarufin is assigned. 100 grams oxybenzoic acid yield 30 grams of anthraflavic acid, 4—5 grams of metabenzodioxyanthraquinone, and 2 grams of anthrarufin.

Pure anthrarufin may readily be obtained from the crude brownish-black product by sublimation and subsequent recrystallisation from glacial acetic acid. An analysis led to the empirical formula, $C_{14}H_8O_4$. Anthrarufin sublimes readily at 120—130°; is almost insoluble in water, and but difficultly soluble in alcohol, from which it crystallises in yellow iridescent regular quadratic tables (m. p. 280°). It is difficultly soluble in glacial acetic acid, yielding a solution with a slight green fluorescence. It is moderately soluble in benzene, and but little soluble in ether and carbon bisulphide; it dissolves in chloroform, from which it crystallises in prisms. None of the above solutions show any absorption-bands, but only a darkening of the spectrum. It is otherwise, however, when strong sulphuric acid is the solvent. Strong solutions by refracted light appear cherry-red, and by reflected light show a strong scarlet fluorescence. Dilute solutions assume a beautiful carmine-red, but only very dilute solutions give sharply-defined absorption-bands. These colour reactions are extremely delicate. One part of the substance in 10,000,000 parts of sulphuric acid shows an evident carmine-red colour in strata 1 inch thick, while absorption-bands may be observed in solutions that appear colourless. Small quantities of nitric or nitrous acids change the carmine-red into a deep yellow which no longer exhibits any absorption-bands. Anthrarufin dissolves in potash-solution with a greenish-yellow colour; the addition of hydrochloric acid produces an orange-coloured precipitate, which by boiling with zinc-dust changes to a green fluorescent liquid. It is almost insoluble in sodium carbonate and in ammonia. Alcoholic acetate of lead gives no precipitate in solutions of anthrarufin, but alcoholic copper acetate gives a brownish-red precipitate. Anthrarufin is not attacked by bleaching-powder, and does not produce lakes with alumina or oxide of iron. It yields a nitro-derivative.

α-Diacetyldioxyanthraquinone, $C_{14}H_6(C_2H_3O)_2O_4$, is obtained by the action of glacial acetic acid on anthrarufin at 200°. It crystallises in yellow needles (m. p. 245°, with decomposition) which are completely insoluble in potash-solution, very difficultly soluble in alcohol, but more readily in glacial acetic acid.

Anthrarufin, when boiled with potash-solution, gives, at a certain concentration of the solution, a brownish potash salt crystallising in needles. By further evaporation, however, an indigo-blue salt is obtained, which on addition of water is again converted into the brown-red modification. Finally, if the mass be heated to fusion, a dark-blue lustrous mass is produced, which dissolves in water with a violet-blue colour. After the removal of unattacked anthrarufin, a yellowish-brown substance is obtained on addition of hydrochloric acid, which on sublimation yields small red needles, consisting apparently of trioxyanthraquinone. They are soluble in potash solution with an indigo-blue colour, and in strong sulphuric acid with a violet colour. Alcoholic lead acetate gives a violet-blue precipitate, and alcoholic copper acetate a blue solution. The determination of the constitution of this body is deferred until a larger amount of material has been prepared.

Attempts to obtain meta-benzodioxyanthraquinone and anthrarufin from oxybenzoic acid in large quantity by the use of means other than sulphuric acid have, as yet, been unsuccessful. T. C.

Detection of Small Quantities of Fluorene in presence of Phenanthrene and Anthracene. By R. ANSCHÜTZ (*Deut. Chem. Ges. Ber.*, xi, 1216—1217).—15 grams of the substance to be tested are oxidised in the ordinary manner with potassium dichromate and sulphuric acid; after six hours' boiling the solid products of oxidation are filtered off and distilled with steam. The distillate by slow crystallisation from alcohol yields, together with unoxidised hydrocarbons, compact crystals of diphenylene ketone if fluorene be present in the original mixture. These crystals can easily be separated mechanically and obtained pure by recrystallisation. T. C.

Examination of the "Gum" of the Quebracho Colorado (*Loxopterigium Lorentii*, Grisebach). By PEDRO N. ARATA (*Anales de la Sociedad Cientifica Argentina*, July, 1878).—This tree, belonging to the Anacardiaceous order, is indigenous in, and peculiar to, the northern part of the Argentine Republic. The so-called gum, or rather thickened juice, collects in the cracks and hollows of the wood, in ruby-red concretions somewhat resembling colophony, but more brittle; it is easily pulverised, and yields a brick-red powder. It is scentless, but has a slightly astringent taste. Sp. gr. 1·3756 at 15°. It is easily soluble in alcohol, acetone, and acetic ether; dissolves also in amyl alcohol, and acetic acid, but is insoluble in benzene, carbon bisulphide, chloroform, and turpentine oil; nearly insoluble in cold water and in ether; nevertheless an ethereal solution, having an emerald-green colour, may be obtained by agitating the gum with ether and water. Boiling water dissolves it completely, and deposits part of it on cooling. It dissolves also in strong sulphuric acid, and is precipitated therefrom by water. Heated in a platinum capsule it swells up and burns, leaving a shining porous cinder, which burns away slowly on continuing the heat. If the combustion be completed in a stream of oxygen, the unburnt residue is scarcely appreciable.

A 1 per cent. solution of the gum in absolute alcohol, in a layer 7 mm. thick, exhibits an absorption-spectrum having a dark band commencing between the solar lines A and B, and terminating at C; another extending for a short distance on each side of D; and a third beginning half-way between D and E and extending to all the more refrangible part of the spectrum. The same solution in a layer 25 mm. thick absorbs the whole of the spectrum, excepting a narrow space from C half-way to D. A solution of dragon's blood, which in some respects resembles quebracho gum, exhibits a very different spectrum, containing a dark band extending for a short distance on each side of C, and a second beginning just beyond D and occupying all the rest of the spectrum.

Reactions.—Quebracho gum, subjected to dry distillation, yields between 100° and 120° a distillate which remains liquid on cooling, and between 240° and 245° a distillate, which solidifies to colourless prisms of pyrocatechin (m. p. 105° nearly, b. p. 240°—245°). The gum is strongly attacked by concentrated *nitric acid*, and when heated with the same acid somewhat diluted with water, it is oxidised to oxalic acid and trinitrophenol or picric acid. Fused with *potash* it yields protocatechuic acid, $C_7H_6O_4$ or $C_6H_3(OH)_2.COOH$, and phloroglucin, $C_6H_6O_3$.

The formation of these products renders it probable that quebracho gum contains one of the bodies called catechins*; but in consequence of the great tendency of these bodies to alteration, the author has not yet been able to obtain satisfactory evidence of their actual presence in the gum. The existence of a catechin in an anacardiaceous plant would be a novelty, these bodies having hitherto been found only in the leguminous, rubiaceous, and cedrulaceous orders. H. W.

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* Gautier has shown that the term "catechin," usually supposed to denote a definite proximate principle of plants, really includes several compounds forming a natural family of organic bodies (see this Journal, 1877, ii, 892).

Chlorophyll. By A. H. CHURCH (*Chem. News*, xxxviii, 168).—Chlorophyll was extracted with ether from the dried leaves of a red-leaved variety of garden beetroot; the ether was removed and the residue extracted with cold alcohol. The alcoholic solution was evaporated over sulphuric acid *in vacuo* in the dark, and the residue on standing assumed an olive-brown colour. This was heated in a water-bath with zinc-dust, when it assumed a bright green colour, and its alcoholic solution gave the red fluorescence and spectral bands characteristic of chlorophyll. The green mass was distilled in presence of zinc-dust in a current of dry hydrogen, when an oily distillate was obtained which appeared to be a mixture of three substances, possibly hydrocarbons; the less volatile portion crystallised on cooling.

L. T. O'S.

Colouring Matter of Wines. By A. GAUTIER (*Compt. rend.*, lxxxvi, 1507—1510).—*Carignane grape.*—Six kilograms of grape-skins were digested in alcohol at 85° and the clear liquor precipitated by the addition of powdered lead acetate. The deep blue precipitate was washed, dried at 60° in an atmosphere of carbon dioxide, and subsequently treated by the method devised by M. Glénard for the preparation of œnolin (*Ann. Chim. Phys.* [3], liv, 360). The substance thus obtained was a violet-red powder, almost insoluble in water and ether, but dissolving in alcohol with a magnificent carmine-red colour. It gave on analysis numbers which agree with the formula $C_{21}H_{20}O_{10}$.

A blue nitrogenous substance in combination with iron also exists in this grape. It was separated by partially neutralising the wine with sodium carbonate, and then adding an excess of common salt. The indigo-blue precipitate, after washing with alcohol, ether, and water saturated with carbon dioxide, was decomposed by shaking with ether containing a little hydrochloric acid, whereby ferrous chloride was formed, and a red acid liberated which dissolved in the ether. The analysis of the iron salt gave the formula $C_{63}H_{60}FeN_2O_{30}$, which is very nearly the triple of the preceding formula.

Grenache grape.—By a similar process to that adopted in the case of the *carignane* grape, a deep violet-red colouring matter was extracted, which on analysis was found to be represented by the formula $C_{23}H_{22}O_{10}$. M. Glénard has also extracted from the *gamay* grape a similar colouring matter, which corresponds with the formula $C_{20}H_{20}O_{10}$.

The author is of opinion that all these colouring principles are derived from a colourless tannic acid, which, in contact with air, becomes red instantly by oxidation. He has moreover succeeded in extracting the colourless tannic acid from the skin of the unripe grape.

J. W.

Gnoscopine. By T. and H. SMITH (*Pharm. J. Trans.* [3], ix, 82).—In the mother-liquors from the purification of narceine, a crystalline alkaloid has been discovered characterised by forming readily crystallisable salts which have an acid reaction. This substance, gnoscopine, $C_{34}H_{36}N_2O_{11}$, is soluble in 1,500 parts of cold alcohol, melts at 233°, but decomposes at the same time. It is insoluble in both aqueous and alcoholic solutions of soda, but soluble in chloroform and carbon bisulphide, and slightly in benzene. The solution of the chloride gives a buff-coloured precipitate with potassium platinochloride. It likewise dissolves in sulphuric acid with a slightly yellow colour, which becomes carmine-red on the addition of a trace of nitric acid. This reaction serves to distinguish gnoscopine from rhœadine, which becomes red on addition of sulphuric acid alone.

E. W. P.

Quinine and Cinchonine. By A. BUTLEROW and WISCHNEGRADSKY (*Bull. Soc. Chim.* [2], xxx, 26).—By the action of alkalis on cinchonine, quinoline (b. p. 243°) is formed, together with a solid substance, which, when treated with alkali gives an alkaloïd of the pyridine series and various volatile acids. The alkaloïd boils at 170—175°. The volatile acids consist of acetic, butyric, and proprionic acids, recognised by the composition of their silver salts (see next paper).

Quinine, subjected to the action of alkalis, gives a liquid alkaline substance boiling about 40° higher than quinoline, and forming an easily crystallisable non-deliquescent hydrochloride, while quinoline hydrochloride crystallises with difficulty and liquefies on exposure to the air. In the second phase of the reaction with alkalis, a volatile alkaloïd and volatile acids are produced, apparently identical with those obtained from cinchonine under the same circumstances.

The authors intend to study the above reactions, and the other transformations of quinine and cinchonine (except their oxidation-products), with the view to determine their constitution.

C. W. W.

Note on the preceding Paper. By M. LUBAVIN (*Bull. Soc. Chim.* [2], xxx, 28).—The author obtained, by the action of alkalis on cinchonine under conditions different from those employed by Butlerow, a series of volatile acids, some more complex than butyric acid.

C. W. W.

Conchinine Sulphate. By O. HESSE (*Deut. Chem. Ges. Ber.*, xi, 1162—1166).—Conchinine sulphate does not, as Petit (Meeting of the Pharm. Soc., Paris, 9 Jan., 1878) and de Vry (*Pharm. J. Trans.* [3], viii, 745) have stated, occur in the anhydrous state in commerce, but contains water of crystallisation, thus: $2C_{20}H_{24}N_2O_2.SO_4H_2 + 2H_2O$, the error of the above-named chemists being due to the fact that they determined the water at 100°, whereas conchinine sulphate loses its water of crystallisation only at 120° and in moist air readily takes it up again. In these respects it differs essentially from quinine, cinchonidine, and cinchonine sulphates, which easily lose their crystallisation water at 100°, and also from homo-cinchonidine sulphate, which gives up its water at the ordinary temperature.

The method proposed by de Vry for testing the purity of conchinine sulphate is identical with that described by the author (*Annalen*, clxxvi, 322). It does not answer, however, in case of adulteration with inorganic salts, but these can easily be detected by treating 1 gram of the salt with 7 c.c. of a mixture of 2 vols. of chloroform and 1 vol. of alcohol (97 per cent.), when complete solution takes place if the sulphate be free from inorganic impurities.

The presence of cinchonidine sulphate in conchinine sulphate can also be detected by treatment with pure chloroform, in which the former is very difficultly soluble; if, however, only a very small quantity of the impurity be present it will dissolve in the chloroform, in which case the chloroform solution must be shaken with cold water, when the whole of the cinchonidine as well as a part of the conchinine sulphate dissolves in the water; the presence of the former sulphate can now be detected by Rochelle salt.

The solution of pure conchinine sulphate in chloroform is at first colourless, but after long keeping in the dark, or exposure to diffused light, it becomes yellow, with a slight green reflex. In direct sunlight, however, after a few hours it becomes cloudy and deposits a small quantity of an amorphous body, the liquid becoming brown. By shaking with water the solution is decolorised in the first two cases, the colouring matter passing into the water, which now exhibits a feebly acid reaction and blue fluorescence. The solution which has been exposed to direct sunlight is not completely decolorised by agitation with water, but the latter becomes more acid than in the former cases. During these reactions the alkaloïd apparently suffers no essential change. The author believes that the reactions are due to the sulphate, dissolved in chloroform, being partially decomposed by direct sunlight into free base and an acid salt. T. C.

On Albumin. By DANILEVSKY (*Bull. Soc. Chim.* [2], xxx, 23). —By the action of alkalis on albumin, an alkaline sulphide, and a substance which the author names *protalbin*, differing entirely from albumin, are formed. Protalbin is reconverted into albumin by heating it several times in sealed tubes with alcohol at 100°.

C. W. W.

Researches on Peptones. By A. HENNINGER (*Compt. rend.*, lxxxvi, 1413—1416).—Peptones, the ultimate products of peptic digestion, have hitherto been found difficult to obtain in a state of purity, owing to their tendency to retain mineral salts or bases, and have yielded on incineration from 3 to 7 per cent. of ash. Maly obtained a fibrin-peptone, which yielded only 0·64 per cent. of ash, by separating the mineral substances by diffusion. The author proposed to attain the same end, by starting with albuminoïds free from mineral matter, and using subsequently only such reagents as could be completely removed by precipitation; substituting, therefore, sulphuric for hydrochloric acid, he found the process required two or three times as long for completion, but the acid could then be exactly removed by baryta.

The pepsin used was of three kinds, an aqueous solution dialysed from a dog's gastric juice, a glycerin solution obtained by Wittich's method, and a very active commercial pepsin. The albuminoïd matters were free from mineral matter, as detailed below.

Fibrin.—The substance, after having been soaked in water containing 1 per cent. of hydrochloric acid, was tied up in a cloth, gently expressed, and hung in distilled water, which was constantly changed; the mass in the cloth was frequently kneaded and squeezed; and all the acid and the salts rendered soluble by the acid were thus removed in the course of three or four days. The gelatinous mass was then thrown into absolute alcohol, which was changed several times; the fibrin, after a final prolonged treatment with ether, to remove fatty matters, did not yield more than 0·29 per cent. of ash.

Albumin, purified by dialysis, yielded only 0·48 per cent. of mineral matter.

Casein.—Skimmed milk was mixed with $\frac{1}{200}$ of soda solution and freed from fat by four successive treatments with ether; the product was then partially neutralised with dilute phosphoric acid, and mixed with a little hydrocyanic acid to hinder putrefaction. This liquid was subjected to dialysis for twelve days, changing the water twice a day; the casein was then separated by adding acetic acid and boiling, and was washed with water.

The purified albuminoïd matter is heated at 44°, with five times its weight of water containing $\frac{3}{1000}$ of H_2SO_4, and the quantity of pepsin requisite to secure rapid digestion. After three or four days, the liquid is filtered, freed from all its sulphuric acid by baryta, and evaporated at 60—70°. Alcohol is gradually added to the syrupy residue, until the liquid becomes turbid and separates on standing into two layers; the lower consists of a little impure peptone, and contains the greater part of the colouring matters. The upper layer is poured in a fine stream into six times its volume of 98 per cent. alcohol, which is meanwhile vigorously stirred; the peptone which settles down is dissolved in a little water, and reprecipitated by alcohol, and this process is repeated. The peptone is then treated with absolute alcohol, first cold and then warm, and finally several times with ether. These treatments with alcohol and ether render insoluble a small quantity of albuminoïds, which remain as a residue on redissolving in water; one more precipitation with alcohol yields a peptone perfectly soluble in water. A trace of impurity, detected by a slight turbidity being produced with acetic acid and potassium ferrocyanide, can be entirely removed by dialysis continued for about ten days. A small quantity of perfectly pure peptone was thus obtained.

The peptones prepared from fibrin, albumin, and casein are amorphous, infusible, white powders, very soluble in water and in glacial acetic acid. They behave like feeble amidated acids. In an acetic solution of the peptones, sulphuric, hydrochloric, or nitric acid produces at once an abundant white precipitate, consisting of a salt of the peptone, corresponding to the acid used. The different peptones show no difference in their reactions; they differ from albuminoïds in being less easily coagulated and precipitated; they very nearly resemble gelatin, but their hot solutions do not set on cooling. The peptones prepared from albumin, fibrin, and casein show different rotatory powers, that from albumin causing least, and that from casein most rotation. So long therefore as the albuminoïds which differ in their rotatory power are allowed to be different varieties, we must also admit the existence of varieties of peptones. F. C.

Physiological Chemistry.

Digestion in Sheep. By E. WILDT (*Landw. Versuchs.-Stat.*, xxii, 54—58).—The amount of the secretion poured into the alimentary canal is very large in comparison with the food eaten, but the greater part of it is reabsorbed. Characteristic secretions are poured in by various glands, and it appeared of interest to ascertain the quantity and relation of the various constituents supplied by the different glands; and also the differences, if any, at various intervals of time after feeding. The food of ruminants usually contain much silica, and as the tissues and liquids of animals are very poor in this substance, it may be assumed that this substance is almost indigestible, and may be therefore used as a standard of comparison in examining the contents of the alimentary canal.

	Contents of section preceeding the rennet-stomach compared with the food taken in 24 hours.	Contents of rennet-stomach compared with the preceding.	Contents of the small intestine compared with the rennet stomach.	Contents of the intestinum rectum compared with those of the small intestine.
Sheep No. I.	gr.	gr.	gr.	gr.
Nitrogenous matter (= 6·25 times N found)	+ 22·707	+ 25·768	+ 22·632	− 63·607
Phosphoric acid.........	+ 7·076	+ 0·185	+ 3·440	− 8·546
Potash	− 2·819	+ 1·666	− 3·745	− 8·023
Soda	+ 13·608	+ 2·983	+ 15·871	− 20·868
Lime..................	− 0·642	− 1·284	+ 1·415	+ 0·185
Magnesia	− 0·741	+ 0·109	+ 0·719	− 0·632
Water	+1162·464	+1993·554	+1484·404	− 446·940
Sheep No. II.				
Nitrogenous matter......	+ 28·872	+ 44·470	+ 4·982	− 63·946
Phosphoric acid	+ 8·796	+ 2·818	− 2·175	− 6·096
Potash	+ 1·564	+ 5·218	− 4·714	− 5·453
Soda	+ 14·913	+ 7·167	+ 7·069	− 17·308
Lime..................	− 0·160	− 0·803	+ 0·107	− 0·172
Magnesia	− 0·514	− 0·140	+ 0·568	− 0·782
Water	+1595·313	+3086·875	+5154·432	−9537·998
Sheep No. III.				
Nitrogenous matter......	+ 16·304	+ 103·231	− 92·963	− 24·779
Phosphoric acid	+ 5·271	+ 8·818	− 8·538	− 3·253
Potash	− 2·254	+ 9·562	− 6·868	− 3·978
Soda	+ 12·532	+ 20·458	− 1·666	− 24·132
Lime..................	− 0·911	+ 0·519	− 0·314	+ 0·216
Magnesia	− 0·745	+ 0·588	− 0·196	+ 0·097
Water	+2023·134	+9485·434	−6462·193	−4263·678

Three sheep were taken and fed with chopped barley straw and distilled water. At the end of about 10 days No. III was killed, 12 hours after the last meal, taken at 6·0 p.m. the day before. II and III were fed at 6·0 a.m.; II was killed at 7·0 a.m., and I was killed at noon, or 6 hours after feeding. The whole alimentary canal was divided into sections, the contents of which were weighed, both before and after drying; the amount of cellulose and nitrogen was then determined for each, and a complete analysis of the ash was made. The numbers thus found are calculated on the amount of food taken during 24 hours, and the results obtained are compared with the constituents of the food taken. The results are given in the table (p. 991); the sign (+) prefixed indicates that in the corresponding section more has been secreted than absorbed; the (—) sign indicates that more has been absorbed than secreted in that section.

The excess of nitrogen, phosphoric acid, soda, and carbon in the first column must be due to the salivary glands; the excess in the second column will be due to the glands of the rennet stomach, and column 3 shows the secretion due to the liver, pancreas, and Lieberkuhn glands. According to these results, the salivary gland is least active in the fasting condition, and increases after feeding; the glands of the stomach are most active during fasting, whilst the glands of the small intestine resemble the salivary glands.

Whilst the food taken is rich in potash, the secretions consist largely of soda, which amounts to 30 times the amount taken as food; the secretion of phosphoric acid reaches 12 times, and that of nitrogenous substances 3 times; these substances are for the most part reabsorbed in the *intestinum cœcum*. J. T.

Work and Digestion of a Horse. By O. KELLNER (*Landw. Versuchs.-Stat.*, xxii, 78—79).—A horse was worked 13—14 days at a time on five occasions, under known loads. The results show that the varying loads had *no* influence on the amount of food digested. The nitrogenous constituents of the urine were also determined, and it was found that an increase of the load was accompanied by a not inconsiderable increase in the amount of nitrogen secreted by this means. J. T.

Influence of Food on the Formation of Bone. By J. LEHMANN (*Landw. Versuchs.-Stat.*, xxii, 58—59).—The author has ascertained, by experiments on young animals, that food containing an insufficiency of phosphates has a decided influence on the various parts of the skeleton. A young pig, which had been fed for 126 days on potatoes only, suffered in consequence from rachitis, whilst other pigs from the same litter, supplied with phosphates, had a normal skeleton. But in the latter case the nature of the phosphate supplied affected the skeleton. Two pigs, supplied with potassium phosphate, had bones which were porous, and specifically lighter than others which were fed with these salts, together with calcium phosphate and carbonate. J. T.

Cow's Milk. By SCHREINER (*Landw. Versuchs-Stat.*, xxii, 60—64).—On boiling milk, hydrogen sulphide is evolved, and can be easily detected in the usual way.

Boiled milk does not coagulate spontaneously so soon as unboiled milk; whilst, on the contrary, boiled milk requires 10 to 12 per cent. more acid to coagulate it than unboiled milk does. The amount of rennet which serves to curdle fresh milk is insufficient to curdle one-tenth the amount of boiled milk, even when applied ten times as long, and at the same temperature (35° C.). The time required for spontaneous coagulation of fresh milk, and the amount of acid required to produce the same effect, depend on the amount of solids in the milk. Unboiled milk treated with rennet curdles the sooner, the less the amount of total solids. The amount of acid required to coagulate milk from the same animal increases in the time from the last calving up to the subsequent dry period, with the increase of the total solids during the lactation period. Milk from Friesland cows gave an increase of solids during this period of from 11 to 13 per cent., whilst that from Simmenthal cows gave an increase from 12 to 16 per cent. Crosses between the two breeds gave milk which sometimes approached the one, and sometimes the other in the amount of increase.

J. T.

Separation of Ammonium Chloride in the Urine of the Dog. By L. Feder (*Zeits. f. Biologie*, xiv, 161—189).—The general result of the author's former experiments has been noticed in this volume (p. 237). Experiments detailed in the present paper confirm that result, viz., that the whole of the ammonia of the ammonium chloride administered finds its way, as such, into the urine and excrement, and that none of this ammonia is converted into urea.

The experiments were carried out on a large dog, which was fed on a meat diet for four days; the average amount of chlorine and of ammonia excreted per day being ascertained, the dog was left to fast for one day, after which it was fed upon meat containing, each day, 5 grams of sal-ammoniac: the amounts of urea, chlorine, and ammonia in the urine, and of the two latter bodies in the fæces, were determined daily. A dose of common salt was administered on the last day of the experiments, in order to drive out the last trace of ammonia from the system. Of the total ammonia administered, 96·7 per cent. was recovered in the urine, and 2·3 per cent. in the fæces. The ammonia was retained in the system for considerable periods, the whole not having passed into the urine until after the expiration of five days. The proportion between the ammonia and chlorine in the urine was generally different from that in which those substances are present in ammonium chloride; the whole of the chlorine administered was not recovered in the urine, about 28 per cent. remaining in the system some days after the experiments were concluded.

The author's experiments seem to establish the fact that when ammonium chloride is administered to dogs, the salt is retained in the system for some time, and is then partially decomposed, the ammonia being combined with other acids, especially with phosphoric acid, and being then passed into the urine and fæces, while the greater part, but not the whole of the chlorine, passes into the urine in the form of alkaline chloride.

During the experiments the amount of urea excreted in the urine increased, the average amount excreted being 21 per cent. greater than the average amount under conditions of normal diet. This increase is traced by the author to an increased decomposition of albumin from the animal's body, under the influence of the ammonium chloride.

A few experiments upon the action of common salt confirmed the general result already mentioned; it was found that common salt is retained in the organism of a dog, especially of a dog which has fasted for some time previously; that the salt is decomposed, and that the sodium is more slowly excreted than the chlorine.

The author criticises, at length, Salkowski's experiments and criticisms upon the author's previous work (*Zeits. f. Phys. Chemie*, vol. i, Part i, p. 52). He objects to the use of small animals; Salkowski experimented with rabbits. The general method of experiment pursued by the latter chemist was unlikely to lead to comparable results; he did not determine both chlorine and ammonia, nor did he make estimations of either of these bodies in the fæces. Salkowski placed reliance upon the amounts of sulphur and nitrogen found in the urine, but he did not determine with sufficient care the proportion between those elements in the various foods administered. For details of the author's criticism the original paper must be consulted.
M. M. P. M.

Diffusion of Salicylic Acid in the Animal Economy. By C. LIVON and J. BERNARD (*Compt. rend.*, lxxxvii, 218—219).—This is a physiological paper on the diffusion and elimination of sodium salicylate in the animal economy. After the lapse of from 1 to 4 hours it was detected in the saliva, the bile, the pancreatic fluid, and in the milk. In all the experiments (dogs being the animals operated on) salicylic acid was detected in the cephalo-rachidian fluid. The presence of salicylic acid was ascertained by treating the substance with hydrochloric acid, then agitating with ether, and adding ferric chloride to the ether residue in order to obtain the characteristic violet reaction.
A. J. C.

Physiological Action of the Hypophosphites. By PAQUELIN and JOLY (*Compt. rend.*, lxxxvi, 1505—1506).—Some time ago the authors showed that the pyrophosphates pass through the system unchanged, that they may be found in the urine as pyrophosphates, and that consequently they cannot be considered as reconstituents, but only as diuretics. They now show that the physiological action of the hypophosphites is precisely analogous to that of the pyrophosphates.

The urine of a patient was carefully analysed for five successive days in order to determine its normal phosphatic value, after which 1 gram of sodium hypophosphite was administered per day. The quantity of urine was increased from 1135 to 1205 c.c., and its density from 1024 to 1029. The mean quantity of urea excreted was slightly increased, while the whole of the hypophosphite was found in the urine unchanged. The authors are therefore of opinion that the hypophosphites act only as diuretics.
J. W.

Absorption of Carbon Monoxide by the Blood. By N. GRÉHANT (*Compt. rend.*, lxxxvii, 193—195).—The author has ascertained the proportion existing between the volume of carbon monoxide which is absorbed by 100 c.c. of blood, and the volume of the gas present in 100 c.c. of an atmosphere of known composition inhaled by an animal during a certain period. The exhaled air was in every case removed from the air inhaled, and the volume of carbon monoxide absorbed was determined by taking the difference between the volume of oxygen which the blood was capable of absorbing before and after inhaling the mixed atmosphere.

100 c.c. of the blood of a dog which had inhaled for 22 minutes an atmosphere containing 1 per cent. carbon monoxide had absorbed eleven times more than the volume of carbon monoxide which was present in 100 c.c. of the air inhaled, *i.e.*, 100 c.c. of blood had absorbed 11 c.c. of CO; similarly continuing the experiments—

	p.c.	The vol. of CO present per 100 c.c. inhaled.		Vol. of CO absorbed by 100 c.c. of blood.
Inhaling for 52 min. an atmosphere containing	0·54 CO gave	1	:	28
Inhaling for 30 min. an atmosphere containing	0·20 „	1	:	50
Inhaling for 70 min. an atmosphere containing	0·10 „	1	:	100
Inhaling for 45 min. an atmosphere containing	0·05 „	1	:	94
Inhaling for 60 min. an atmosphere containing	0·025 „	1	:	48

A. J. C.

Chemistry of Vegetable Physiology and Agriculture.

Theory of Fermentation. By PASTEUR; reply by BERTHELOT (*Compt. rend.*, lxxxvii, 125—129).—The views expressed in the following laboratory notes by the late Claude Bernard, which have been published by Berthelot as the last experiments of Bernard on alcoholic fermentation, condemn without any restriction the opinions held by Pasteur. It is, however, believed by Pasteur that these notes are merely the outlines of work which was intended to be pursued, and are not conclusions from actual observations, as he has strong reasons to believe that Bernard accepted his theory on alcoholic fermentation. Bernard says that—

1. Alcoholic fermentation is not life without air, for alcohol is formed by contact with air without yeast.

2. The ferment is not derived from external germs, for in sterile juices the ferment is not developed, although the juices may be saccharine. Fermentation ensues on adding the ferment.

3. Alcohol is formed by a soluble ferment apart from the life in the ripening fruit; there is then decomposition of the fruit and not a

biosic synthesis of the yeast. Air is absolutely necessary for this alcoholic decomposition.

4. The soluble ferment is found in the juice expressed from the fruit; there the alcohol continues to form and to increase. This action is more easily manifested by using an infusion of old yeast.

5. In fermentation there are two conditions to study, viz., decomposition and morphological synthesis.

Berthelot, in reply to Pasteur, states that he believes these notes truly express the conclusions which Bernard had deduced from his last experiments on alcoholic fermentation. A. J. C.

Unorganised Ferment in Plants. By C. KRAUCH (*Landw. Versuchs-Stat.*, xxii, 77—104).—The author, after noticing results obtained by other investigators, gives a detailed account of his own work. For the preparation of the ferments, water holding salicylic acid in solution was used, and direct experiment on malt showed that the action of the ferment obtained was not prejudiced by the salicylic acid. The experiments were mainly confined to the fatty oils, starch, and albumin of plants. But besides these, the action of ferment-solution on gum arabic, emulsion of quince, and the glucosides salicin and amygdalin was studied. Diastase-ferment of malt, maize, sprouting onion, and pumpkin were added to gum-solution, and, after 24 hours, a liquid reducing Fehling's test was obtained in each case. The same four ferments exercised no action on quince emulsion. The glucosides were treated with ferment from maize, pumpkin, white-thorn, and oak leaves. After 12 hours, the only sugar reaction obtained was with pumpkin-ferment on salicin. After 48 hours, however, a faint sugar reaction was obtained with the ferment from oak-leaves and amygdalin. Some malt-diastase was carefully prepared by Duquesnel's method and analysed. It was obtained as a light-yellow powder soluble in water to a clear solution; it contained a small quantity of sulphur which was not determined. Two carbon, hydrogen, and ash estimations gave—

	(1.)	(2.)	
C........	45·64	45·73	per cent.
H........	6·90	6·89	„
Ash......	6·00	6·16	„

The nitrogen estimations gave 4·60, 4·54, and 4·55 respectively. The mean result is CO_2 45·68, H 6·90, N 4·57, ash 6·08, O(S) 36·77 = 100. Diastase differs from pancreas-ferment in that, even after standing a long time over sulphuric acid, it still gives off water when heated. It loses 5·88 per cent. when heated to 100° C. for several hours, and at 125° it loses 7·6 per cent. of its weight. Pancreas ferment, which has 9·5 per cent. more nitrogen, is said not to lose water on heating to 100° (Hüfner (*Jour. f. pr. Chem.* (N.F.), v, 377), but both the ferments lose their active properties when heated to 75—80 in solution, although they bear a temperature of 100° when in the dry state. An analysis of a less pure diastase, which was soluble in glycerin but only partly so in water, gave C 55·58, H 8·24, N 6·13, ash 4·46, (S)O 25·29 = 100. This was prepared by extraction with glycerin, and it appears that less ash-forming constituents were extracted than by water with salicylic acid, but that more organic impurities are present.

The results obtained as to the occurrence of ferments are shortly given as follows:—

1. Ferments capable of decomposing fat and digesting albumin could not be detected in any case.

2. Diastase ferments. *a.* A very active ferment is present in the young wood of the horse-chestnut, both when the circulation is active and in repose. A feeble ferment is contained in the leaves of the white-thorn and of the oak. The birch is free from diastase.

b. Onions and potatoes contain a feeble ferment. But only the onion affords it when the plants are resting.

c. Fruits rich in starch. Barley contains diastase, but it is less active than the diastase obtained after malting. In ungerminated maize, the diastase is almost confined to the germ and the cotyledon.

d. Oily seeds. Ungerminated pumpkin seed contains a feeble diastase; the germinated, a somewhat stronger one.

Diastase is somewhat widely diffused in organs containing starch, on the one hand occurring plentifully in parts rich in starch, and on the other hand occurring sparsely in parts poor in starch. Diastase occurs at times in organs at rest, and at times only when the plant-organ is growing. Sometimes a plant at rest contains a little diastase, sometimes it does not appear until the commencement of vegetation. But the conversion of starch into glucose does not invariably occur when diastase is present, as is seen in the case of the birch, which, in spite of its richness in starch, did not give any indication of the presence of diastase at any time. It is possible that the conversion and solution of starch in these cases may be effected by the acids of the plants.

J. T.

Influence of Leaves on the Production of Sugar in the Beet. By Corenwinder and Contamine (*Compt. rend.*, lxxxvii, 221—222).—Corenwinder has previously shown (this Journal, 1877, i, 336) that the amount of sugar in beets varies in direct proportion to the size of the leaves—beets having the largest leaf-surface containing the most sugar. The authors find that there is no exception to this law, which is probably due to the well-known fact, that carbon dioxide is decomposed in proportion to the extent of leaf surface which is presented to atmospheric action.

Presence of Sugar in the Leaves.—Continuing the examination of this question, and confirming Corenwinder's statement that the chief part of the sugar in the leaves is confined to the mid-rib, where it exists, as stated by Dehérain, as a mixture of glucose with a small quantity of crystallisable sugar, it is now found that the proportion of sugar is much less in the secondary nerves of the leaves, and still less in the parenchyma. It is not contended that the sugar which is present in the nerves of the leaves has been elaborated in those organs.

A. J. C.

Amounts of Sugar contained in the Nectar of Various Flowers. By A. S. Wilson (*Chem. News*, xxxviii, 93).—The sweet-tasted fluid which is secreted within the cups of insect-fertilised flowers is called nectar, and the object gained to the plant by its presence is that insects, induced to visit flowers for its sake, are useful to the plants by effecting a cross-fertilisation. In many instances this sweet liquid is exuded from special glands, but in other cases from portions of the flower which do not seem to have been specially adapted for this purpose. It is a point in dispute amongst biologists whether this saccharine matter is a true secretion, or simply an excretion of effete matter from the vegetable cells—a bye-product of the chemical changes taking place within the cells. The latter view seems to be favoured by the fact that a similar sweet-tasted fluid, much sought after by insects, is exuded on different parts of some plants quite unconnected with the flower, as in the laurel, brake, fern, lime tree, acacia, &c. The bright colours, as shown by Lubbock's experiments, serve to guide insects to the flowers, and the odours which they emit fulfil the same end. The importance of these guides to insects will be apparent from the following estimations, which show how indispensable it is that as little time as possible should be lost by an insect collecting honey. The formation of nectar is observed to take place most freely in hot weather, and to be prevented by cold or wet. By biologists, the visits of bees, butterflies, and other insects are believed to have exercised in past time an important influence in modifying the size, shape, colour, &c., of flowers, and the following experiments are of interest as showing to what an extent this action takes place in nature, and as helping to determine the value of this factor. The nectar was extracted with water, and the sugar determined, before and after inversion, by means of Fehling's copper solution. In the case of fuchsia—which is not deprived of its nectar by any insect in this country, the nectary being inaccessible to native species—we have probably the whole amount formed, but in other cases the visits of bees, &c., may have reduced the amounts considerably. In this case it is a clear colourless liquid, having an acid reaction and an intensely sweet taste; that of many others has the strong characteristic odour of honey:—

Sugar in Flowers.

	Total mgram.	Fruit sugar.	Cane sugar? (as fruit).
1. Fuchsia per flower	7·59	1·69	5·9
2. *Claytonia Alsinoïdes*, ditto	0·413	0·175	0·238
3. Everlasting pea, ditto	9·93	8·83	1·60
4. Vetch (*Vicia Cracca*) per raceme	3·16	3·15	0·01
5. Ditto, per single flower	0·158	0·158	—
6. Red clover, per head	7·93	5·95	1·98
7. Ditto per floret	0·132	0·099	0·033
8. Monkshood, per flower	6·41	4·63	1·78

Approximately, then, 100 heads of clover yield 0·8 gram sugar, or 125 give 1 gram, or 125,000 1 kilo. of sugar; and as each head contains about 60 florets, 7,500,000 distinct flower tubes must be sucked in order to obtain 1 kilo. of sugar. Now as honey, roughly, may be said to contain 75 per cent. sugar, we have 1 kilo. equivalent to

5,600,000 flowers in round numbers, or say 2½ millions of visits for one pound of honey. This shows what an amazing amount of labour the bees must perform. Another point worth notice in these results is the occurrence of what appears to be cane-sugar, and in the case of fuchsia in the proportion of nearly three-fourths of the whole. This is remarkable, as honey is usually supposed to contain no cane-sugar, the presence of the latter being usually regarded as certain evidence of adulteration. The question therefore arises whether this change, which takes place while the sugar is in the possession of the bee, is due to the action of juices with which it comes in contact while in the honey-bag or expanded œsophagus of the insect, or whether the process of inversion goes on spontaneously, as may perhaps be the case. D. B.

Composition of Potatoes. By J. H. Gilbert and J. B. Lawes (*Chem. News*, xxxviii, 28).—In experimenting on the effects of different manures on the potato, a variation in the amount of produce from something over three tons without manure to nearly nine tons with the highest manure had been obtained. Samples of the different crops had been analysed in the usual way, and a great difference in the composition of the tubers was found. It occurred to the authors that it would be interesting also to examine the tubers somewhat in the way adopted in the case of some root-crops, such as sugar-beet, that is, to express and determine the composition of the juice. It was found that by far the largest proportion of both the mineral matter and the nitrogen of the tuber existed in the clear filtered juice, the percentage varying with the character of the manure and the amount of crop. Jellett had already examined the juice, or rather the extract of sound potatoes, of the apparently sound part of diseased potatoes, and of the discoloured part of diseased potatoes. He found a considerable development of sugar in the white part of the diseased tubers. He also determined the amount of nitrogen in the dry matter of similar specimens, and found it to be greater in that of the apparently sound part of diseased potatoes than in that of sound potatoes, and also greater in the diseased part, but not so great as in the apparently sound part. In accordance with these results, the authors found a higher percentage of nitrogen in the dry substance of the diseased than of the sound potatoes; but, calculating the quantity upon the fresh tubers, they did not find evidence that there was an actually greater amount of nitrogen in the diseased potatoes.

The most interesting point in the results was, however, that whilst the juice of the white portion of the diseased potatoes contained approximately the same amount of nitrogen as that of corresponding sound potatoes, the juice of the diseased portion contained very much less, in fact, only about one-half or two-thirds as much. On the other hand, the wasted or exhausted solid matter of the white portion contained a very small amount of nitrogen, whilst that of the black or diseased portion contained very much more, in some cases four or five times as much. It was also found that the amount of mineral matter was much higher in the juice of the white than in that of the diseased part, but much lower in the exhausted part of the white than in that of the discoloured portion. It was obvious from these facts that the juice had suffered exhaustion of much of its nitrogen and mineral matter in the development of the fungus. The sugar, itself the result of diseased action, probably also contributed to the same end.

D. B.

Analysis of Behar Opium Ash. By C. J. H. WARDEN (*Chem. News*, xxxviii, 146).—The ash consisted of a mixture of the ashes of all samples of Behar opium analysed in the Government Opium Factory, Patna. It was of a light grey colour, and contained 0·8575 per cent. of charcoal, which was deducted before calculating its percentage composition, which is as follows:—

Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	SO_3.	P_2O_5.	SiO_2.
1·9839	7·1344	2·3104	37·2405	1·7006	23·1419	10·9021	15·2740

There were also traces of alumina, manganese, carbon dioxide, and chlorine.

The sulphuric acid, of which there is an unusually large quantity present, is considered to be united with the potash and lime. It has been pointed out that the increase of sulphuric acid in a plant is attended with a decrease of morphine. The author suggests that some relation exists between the quantity of sulphuric acid in the plant and its richness in morphia.

L. T. O'S.

Mineral Constituents of Horse-radish. By A. HILGER (*Landw. Versuchs-Stat.*, xxii, 75—76).—The fresh root contained 83·45 per cent. of water. Dried at 100°, 11·15 per cent. of ash was obtained, and this was analysed by Bunsen's method. The ash contained:—sol. in water containing CO_2, 72·52 per cent.; insol. 27·48, in which we have 2·5 per cent. carbon and 2·7 per cent. sand.

The soluble portion contained:—		The insoluble part contained:—	
CaO	1·19	CaO	35·38
MgO	0·89	MgO	11·92
Na_2O	0·28	P_2O_5	41·92
K_2O	51·41	Fe_2O_3	3·47
HCl	2·19	CO_2	7·23
SO_3	22·73	SiO_2	5·39
CO_2	15·31		

J. T.

Composition of a White Deposit in Teak Wood. By G. THOMS (*Landw. Versuchs-Stat.*, xxii, 68—69).—The wood of *Tectonia grandis* not unfrequently contains a white deposit, consisting mainly of phosphoric acid, lime, and water. From the large amount of calcium phosphate present, it was conjectured that the wood itself might be rich in phosphoric acid and lime. An analysis of the ash confirmed this surmise.

	White layer. 1872.	White layer. 1877.
Moisture	5·92	10·40
Phosphoric anhydride	42·30	39·42
Lime	33·24	29·78
Magnesia	—	0·34
Iron oxide	—	0·01
Woody matter insol. in dilute HCl	—	7·84
Water and trace of organic matter	18·54	12·21

	Ash of teak-wood.
Magnesia	9·74
Lime	31·35
Iron oxide	0·80
Potash	1·47
Soda	0·04
Silica	24·98
Sulphuric anhy.	2·22
Phosph. anhy.	29·69
Carbonic anhy.	0·01
Chlorine	0·01
	100·31

The lime, phosphoric anhydride, and combined water above correspond to $(2CaO,H_2O,P_2O_5)$, and the deposit of 1877 contains an excess of 1·67 per cent. of phosphoric anhydride. J. T.

Carbonic Anhydride in Soils. By EBERMAYER (*Landw. Versuchs-Stat.*, xxii, 64—66).—During some investigations, a question arose as to the influence of soil rich in humus, found in woods, on the amount of the carbonic anhydride present in the air and soil in woods. Two series of experiments were made, one in the botanical garden at Aschaffenburg, and the other in a wood of fir and beech at Spessart. At the first place, the carbonic anhydride was determined in the atmospheric air, and also in the air of a barren, unmanured, and uncultivated soil, and also in a tolerably sandy soil growing acacia bushes. In both cases the air was taken from a depth of 1 meter. The wood at Spessart has an eastern aspect, and its subsoil is a sandy clay. The air was taken 2 meters above the soil, 3 meters deep in the soil rich in humus, 0·5 meter deep, and again at a depth of 1 meter. In the neighbourhood of the wood is a meadow, overlying the same formation, which is manured every three years. Samples of ground-air were taken here and examined also. Samples were taken three or four times a month, with the following results:—

Average amount of CO_2 per 1000 ccm.:—

a. In uncultivated soil (1 m. deep);

from Jan. to April	9·87
„ May „ August	23·11
Mean	16·49

b. In similar soil amongst acacia bushes, near to (*a*);

from Jan. to April	4·59
„ May „ August	14·29
Mean	9·44

c. In free atmosphere (2 m. above the ground);	
from Jan. to April........	0·37
„ May „ August......	0·46
Mean........	0·41
d. In the air of the wood (2 m. above the ground);	
from May to August......	0·80
e. In the humus-layer of the soil;	
from May to August......	1·48
f. In the soil of the wood (½ m. deep);	
from May to August......	4·55
g. In the soil of the wood (1 m. deep);	
from May to August......	5·02
h. In meadow land (½ m. deep);	
from May to August......	26·69
i. As in *h*, but 1 m. deep..........	25·63

These results show that—(1.) The air in the wood is almost as rich again in carbonic anhydride as in the open, in summer at least. (2.) Wooded soil is much poorer in carbonic anhydride than unwooded during summer, and meadow land at a depth of 0·5 meter averages six times as much, and at 1 meter five times as much as the soil in a wood. (3.) With increase of temperature, the carbonic anhydride increases much more in meadow land than in forest land, thus:—

	Meadow land.	Forest land.
In May, ½ m. deep..	19·82 parts CO_2 per 1000	3·95 CO_2 per 1000
„ 1 „ ..	17·50 „	4·36 „
In July, ½ „ ..	31·70 „	5·77 „
„ 1 „ ..	32·09 „	6·32 „

(4.) The carbonic anhydride appears to diffuse very slowly, as the difference between two places very near to each other is sometimes considerable (see *a* and *b*). These various results are due to a difference in temperature of the soils in summer, to the greater porosity of the meadow soil, and the more intimate mixture of vegetable matter in the cultivated soil. The small amount of carbonic anhydride present will affect the amount of silicates decomposed in the soil, so that the preparation of food for plants will go on much more slowly in a wood than in cultivated ground. Further, the soil of woods can have no perceptible influence on the amount of carbonic acid and lime in spring waters; under similar conditions unwooded soil would have more effect. This agrees with results obtained by Volger in determining the amount of carbonic acid in spring waters. J. T.

Absorption of Ammonium-nitrogen by Soils and Subsoils. By A. ORTH (*Landw. Versuchs-Stat.*, xxii, 49—53).—The absorptive powers of soils, and also of the various formations occurring beneath them, was the object of this investigation. W. Knop's method was employed: chalk was added to the air-dried soil, which was then treated with a definite amount of ammonium-chloride solution in the cold for two days, afterwards the nitrogen in the non-absorbed ammonium of the filtrate was expelled by treatment with brominated soda-lye. 250 experiments have been thus made; the results are to be published in a separate work; but the following may be noted here:—

Upper Vein-Marl (Gneis Subsoil), Frederichsfelde, near Berlin.

Thickness of layer.		100 grams earth absorb c.c. of nitrogen (from NH_4Cl).
0·25 m.	Clayey sand (ploughed)	26·4 = ·033 gram
0·35 „	„ lower layer	23·0 = ·029 „
0·40 „	Clay of the vein-marl	74·2 = ·093 „
7·0 „	Vein-marl, upper, oxidised and yellow	40·1 = ·050 „
	Vein-marl, middle, oxidised and yellow	41·7 = ·052 „
	Vein-marl, lower, unoxidised and grey	37·3 = ·047 „
	Diluvial sand, containing sand	13·9 = ·017 „

Upper Vein-Marl from Halle-on-Saale.

0·5 m.	Sandy clay containing humus	46·0 = ·0589 gram
0·3 „	Clay of the vein-marl	73·0 = ·092 „
2·0 „	Vein-marl (clay-marl)............	42·5 = ·053 „
	Diluvial sand and gravel	13·0 = ·016 „

Upper Vein-Marl Schulauer Banks, below Hamburg.

0·7 m.	Light clayey sand of the upper vein-marl	16·5 = ·021 gram
0·5 „	Clay of the upper vein-marl	77·0 = ·096 „
	Upper vein-marl (clay marl)......	41·0 = ·051 „

The influence of the disintegration (Schulauer) and the enrichment in humus (Halle) in the crust, also the effect of the increased amount of alumina and iron in the clay above the vein-marl, is very well shown by the above figures; the results obtained for districts far apart are also seen to agree very well. The ploughing of the strongly absorptive clay requires more care than that of the less absorptive clayey marl, or a diminished yield may result. If quick-lime be added at the same time, the strong clay may become as good as the upper soil; but if lime be not added, then the amount of clay which can be advantageously turned up will depend on the material in the upper crust capable of acting upon it.

Diluvial Marl with Layer of Black Earths, Stassfurth, Saxony.

Thickness of layer.		100 grams earth absorb c.c. of nitrogen (from NH_4Cl).
0·6 m.	Black earth (Tschernosem), light clay bottom, with humus	83·0 = ·104 gram
1·0 „	Finer clay marl (highly oxidised and yellowish-grey)	49·5 = ·062 „
	Diluvial sand (lime bearing)	11·5 = ·014 „

Diluvial Clay from Canth, Silesia (as an example of a White Soil).

0·3 m.	Clay soil (ploughed)	53·0 = ·067 gram
1·0 „	Diluvial clay (completely oxidised)	85·0 = ·107 „
	Diluvial gravel (with many porphyry fragments)	20·5 = ·026 „

Very Clayey Vein-Marl, Merde, West Prussia.

0·2 m.	Black earth, clay bottom, with humus (ploughed)	107·5 = ·135 gram
0·8 „	Black earth, stiff clay, with humus	122·0 = ·166 „
	Clay marl (used as cement marl; incompletely oxidised, grey)	116·5 = ·146 „

Loess Marl, from Vienna.

0·5 m.	Limey clay soil..................	71·0 = ·089 gram
1·5 „	Loess-marl, completely oxidised, yellowish-grey	62·5 = ·078 „

Diluvial Marl from Taganrog, Sea of Azov.

0·7 m.	Black earth, clay with humus	107·5 = ·135 gram
5·0 „	Loess-like clay marl (completely oxidised, yellowish-grey)	92·5 = ·116 „
	(Diluvial sand beneath).	

These investigations show—(1) the importance of considering the surface layers as well as the geological formations in their bearing on geographical and practical questions; (2) the fruitfulness of a soil is a very complex quantity, and regard must be paid to many circumstances; still the nitrogen-absorption determination is an excellent means of characterising the changes going on in the soil, especially with respect to the diminution or increase in the amount of clay, iron, and humus. There is often great difficulty in forming a true idea of the condition of a soil from these analytical results. This method of absorption permits changes to be tolerably quickly ascertained in many soils. Two determinations will serve to show how small the change is which may be detected.

In laying bare the roots of some trees in Berlin, the soil amongst the roots was found to have been bleached, while the surrounding soil was yellowish-brown from the presence of iron, showing that iron had been removed. The numbers obtained were as follows:—Spree Valley sand, beyond the action of the roots, 100 grams absorbed 12 c.c. nitrogen; the same bleached, from among the roots, 8·5 c.c. were absorbed. J. T.

Analytical Chemistry.

New Method for Estimation of Sulphur. By C. FAHLBERG and M. W. ILES (*Deut. Chem. Ges. Ber.*, xi, 1187—1190).—Contrary to the results of former investigators, the authors find that sulphur when fused with an excess of alkali does not yield a sulphide (Berzelius, *Jahrb.*, v, 94) or a hyposulphite and sulphide (Döpping, *Ann. Chem. Pharm.*, xlvi, 174; Kersler, *ibid.*, lxviii, 231, &c.), but is converted entirely into sulphite, or with a larger excess of alkali into sulphate and sulphide. These facts are now made the basis of a method for the quantitative estimation of sulphur, both in organic compounds and in sulphides. The method is preferable to that ordinarily employed, viz., oxidation with nitrate or chlorate of potassium, as it is free from the almost unavoidable loss to which the latter process is liable from the violent reaction which occurs. The operation is as follows:—In organic sulphur compounds, 0·1 to 0·5 gram is fused with 25—50 grams of potassic hydrate in a silver crucible until the evolution of gas ceases and the melt becomes tranquil: when cold the mass is entirely soluble in water. The colourless solution thus obtained is decomposed with 75—100 c.c. of bromine-water, when the liquid remains clear and transparent, showing that neither sulphides nor hyposulphites are present. Hydrochloric acid is next added to acid reaction, and the oxygen and bromine are expelled by boiling until the solution becomes colourless. The sulphuric acid present is finally determined by precipitation with barium chloride in the ordinary way.

The sulphur in metallic sulphides is determined as above, except that, where metallic oxides separate out after dissolving the fused mass in water, the liquid must be filtered before bromine-water is added. In the case of volatile sulphur compounds, the sulphur must, previous to fusion, be combined with alkali by heating with strong aqueous alkali in sealed tubes at 120° C.; the contents of the tubes are afterwards carefully removed, the water driven off at a gentle heat, and the mass finally fused as above described. A large number of determinations of sulphur in various organic substances and in sulphides, &c., show that the method gives very good results. T. C.

Determination of Sulphur in Coke. By W. A. BRADBURY (*Chem. News*, xxxviii, 147).—The author relates a number of experiments to show that the amount of sulphur obtained by boiling coke with nitric acid, aqua regia, and potassium chlorate is considerably below that obtained when the coke is fused with nitre, sodium carbonate, and common salt. L. T. O'S.

Indirect Estimation of Hyposulphites (Thiosulphates) and Sulphites. By I. GROSSMANN (*Chem. News*, xxxvii, 224).—In a mixture of hyposulphites (thiosulphates) and sulphites, as in the intermediate and final products in the manufacture of soda-ash and caustic soda, the author has employed with great advantage the following method of analysis:—

I. In the absence of sulphates:—One portion of the solution is acidulated with acetic acid and titrated with iodine in the usual manner, and another portion is oxidised with chlorine or bromine, and the amount of sodium sulphate so formed is ascertained. The results thus obtained give the necessary data for the calculation of the amount of thiosulphate and sulphite respectively.

Let x_I = grams of iodine corresponding to $Na_2S_2O_3$ per cent.
y_I = " " Na_2SO_3 "
A = " used in titration per unit.
B = " Na_2SO_4 per unit after complete oxidation.

Then $x_I + y_I = A$.

$$\frac{2Na_2SO_4}{Na_2S_2O_3} \cdot \frac{Na_2S_2O_3}{I} \cdot x_I + \frac{Na_2SO_4}{Na_2SO_3} \cdot \frac{Na_2SO_3}{2I} \cdot y_I = B.$$

$$\text{Which gives } x_I = \frac{2I}{3Na_2SO_4} \cdot B - \tfrac{1}{3}A,$$

$$\text{and } y_I = \tfrac{4}{3}A - \frac{2I}{3Na_2SO_4} \cdot B.$$

The result in grams of $Na_2S_2O_3$ is obtained by multiplying x_I by $\frac{Na_2S_2O_3}{I}$, whence $x = \frac{2Na_2S_2O_3}{3Na_2SO_4} \cdot B - \frac{Na_2S_2O_3}{3I} \cdot A = 0{\cdot}741784\ B - 0{\cdot}414698\ A$.

Also the amount of Na_2SO_3 by multiplying y_I by $\frac{Na_2SO_3}{2I}$, whence $y = \frac{2Na_2SO_3}{3I} \cdot A - \frac{Na_2SO_3}{3Na_2SO_4} \cdot B = 0{\cdot}661417\ A - 0{\cdot}295775\ B$.

II. In the presence of sulphates:—The amount of sulphate is determined by precipitating with barium chloride in an hydrochloric acid solution, after concentration in an atmosphere of carbon dioxide, and the Na_2SO_4 thus found subtracted from the total Na_2SO_4 by oxidation = B.

Before applying this method, sulphides must be separated by cadmium carbonate. A. J. C.

Volumetric Estimation of Sulphates in Potable Water. By A. HOUZEAU (*Compt. rend.*, lxxxvii, 109).—To 10 c.c. of the water, after acidifying with one drop of acetic acid, a sufficient quantity of a standard solution of barium chloride (30·5 grams per litre) is added, drop by drop, from a dropping tube which gives 25 drops per c.c., until the clear filtrate gives no further cloudiness on adding another drop of the barium chloride solution. A. J. C.

Estimation of Potash and Phosphoric Acid in Commercial Products. (*Chem. News*, xxxviii, 54—55 and 63—65).—*Estimation of Potash.*—Although the process of determining potassium by precipitation with chloride of platinum is the method almost universally adopted by chemists of large experience in the assay of commercial potash salts, it was thought desirable to investigate also the volumetric method of Stolba, which is based on the precipitation of potassium as silico-fluoride, and the titration of the precipitate with standard alkali, according to the equation, $K_2SiF_6 + 4KHO = 6KF + H_4SiO_4$.

A whole series of careful experiments was made, from which it is concluded that this method gives results below the truth, a fact which is probably due to the difficulty of decomposing the last traces of silico-fluoride by alkali without introducing an excess of the latter. The trace of free alkali which suffices to change the tint of the litmus to blue seems incapable of reacting on the silico-fluoride. An attempt was made to overcome this difficulty by adding a sensible excess of alkali, boiling well, and titrating back with standard acid, but the result was not satisfactory, the end of the reaction being very obscure. As the drying and weighing of the silico-fluoride require but little more time than the titration with alkali, and give better results, the gravimetric method is to be preferred, although it is not to be compared in accuracy with the platinum-chloride process. As to the separation of potassium from sodium by precipitating with hydro-fluosilicic acid, experiments have shown that the process is quite worthless.

Methods of determining Phosphoric Acid.—In most cases these are quite free from novelty, but as the evidence collected, and the results of many commercial analyses show that certain considerations and precautions are in many cases partly or wholly neglected, it was thought that the following suggestions would tend greatly to diminish the number and extent of the discrepancies common in determinations of phosphoric acid.

Solution of the Manure.—For dissolving the soluble phosphate contained in a manufactured manure, cold water should be employed, and the treatment and digestion with the solvent should not be extended over more than two or three hours. For the solution of the portion insoluble in water, or for the determination of the total phosphoric acid, hydrochloric acid is the most suitable. In manures containing iron, the addition of a few drops of nitric acid is desirable to ensure the complete peroxidation of any ferrous compound which may be present. In manures containing silica, the evaporation of the acid solution to dryness should never be omitted, as it not merely effects partial elimination of any fluorine that may be present, but also prevents the precipitation of the silica at a subsequent stage of the operation. In cases in which much organic matter is present, iron and aluminium cannot be precipitated satisfactorily. In such cases it is necessary to ignite with an alkaline oxidising mixture previous to the acid treatment.

Separation of the Iron and Aluminium.—If more than traces of these constituents are present they should be separated. In the first place, several of the most satisfactory methods of determining phosphoric acid are vitiated by the presence of these metals; and secondly, the manurial value of the sample is affected by their presence. The removal of these metals from the solution as phosphates is readily effected by neutralising any excess of acid with ammonia and adding ammonium acetate. The operation should be conducted in a cold or but slightly warm solution, otherwise a calcium phosphate is thrown down.

Oxalic Acid Method.—In employing this method it is very desirable to previously separate iron and aluminium phosphate, which renders it unnecessary to add an organic acid before precipitating the phosphate with magnesia.

Direct Citric Acid Method.—In this method the iron, aluminium, and calcium are all retained in solution by means of ammonium citrate, the phosphate being at once precipitated from the ammoniacal solution by magnesia mixture. The sources of error by this method are too numerous to be wholly disregarded, and it appears preferable to titrate the precipitate with uranium instead of direct weighing.

Precipitation with Magnesia Mixture.—Experiments have shown that magnesium chloride used for the precipitation of ammonio-magnesium phosphate is attended with less tendency of error than the employment of magnesium sulphate. A large excess of the precipitating mixture causes a more rapid separation of the double phosphate, but is attended with such a serious tendency to error that any advantage gained is more than counterbalanced. The precipitation should be done in the cold, a large excess of ammonia being present. By previously removing silica, fluorine, iron, and aluminium, it will rarely be necessary to purify the precipitate by solution in acid and reprecipitation with ammonia. If the precipitate be titrated with uranium many of the above precautions are rendered superfluous.

Estimation by Uranium.—This method is based on the removal of iron and aluminium by addition of an alkaline acetate in the cold, with determination of the phosphoric acid in the filtrate by means of a standard solution of uranium. The titration should be *converse*, the solution of the phosphate being added to that of the uranium. Owing to the reversal of the usual process, the brown colour of the ferrocyanide of uranium becomes gradually fainter until the end of the titration.

Molybdic Acid Method.—Sonnenschein's process of precipitation with molybdic acid, with subsequent treatment with magnesia mixture and weighing as magnesium pyrophosphate, is probably the most uniformly accurate of all known processes for determining phosphoric acid; the large excess of molybdic acid, however, renders the method very expensive, as there is no simple process of recovering the molybdenum in the filtrate, and the bulky and unmanageable nature of the precipitate when the quantity of phosphoric acid present exceeds 0·1 or 0·2 of a gram—a fact which leads to the employment of very small quantities of the material—often prevents chemists from generally adopting this method, although in some cases it is simply invaluable.

Reduced Phosphates.—The methods which have been employed for the determination of "reduced" phosphates are based on the ready solubility of such precipitated phosphate in certain liquids, or on its easy decomposition by certain alkaline salts. For its solution, ammonium citrate, and for its decomposition with formation of a soluble phosphate, oxalate of ammonium or bicarbonate of sodium has been used. A series of experiments has led to the conclusion that these methods are quite useless, as reduced phosphates were indicated by each process even in natural phosphatic materials which had never been treated with acid. It is now generally admitted that the cause of the "going back" to the condition of insoluble phosphate is the presence of iron and aluminium in the manure, and many chemists are of opinion that the "reduced phosphates" actually consist of the phosphates of iron and aluminium produced by some such reaction as the following:—

$$CaH_4(PO_4)_2 + Al_2(SO_4)_3 = 2AlPO_4 + CaSO_4 + 2H_2SO_4.$$

The value of a manure depends so largely on the proportion of oxide of iron and alumina present, as to render it necessary to state always the united percentage of these two bases in a manufactured manure (superphosphate). By doing so the manufacturer or purchaser would be enabled to judge of the probability of a newly-made manure "going back" on keeping, and he would be in a better position to form an opinion of the true value of the sample.

At the end of this paper, a table is given with respect to the mode of statement of the results of analyses of commercial phosphates.

D. B.

Detection of Alum in Bread and Flour. By G. WELBORN (*Pharm. J. Trans.* [3], ix, 181).—The author considers that too much allowance has been made for alumina in wheat, as it is not an invariable constituent.

It is recommended to use a dialyser, and to determine the alum in the dialysed liquid by (1) washing, drying, and igniting the precipitated aluminium phosphate; (2) by measuring the volume of the precipitate in a tall, narrow cylinder, and comparing it with that from a known quantity of alum; (3) by comparison and imitation of the degree of opacity with aluminium phosphate, in a similar cylinder and volume of water, obtained from a known measure of a standard solution of alum.

Hydrochloric acid appears to facilitate the process of dialysis, keeps the bread or flour from fermentation, and also prevents the formation of mould. A large excess of free ammonia, or ammonic compounds prevents the ready subsidence of the aluminic phosphate, and is therefore to be avoided. The addition of ammonic chloride up to a certain point causes the rapid separation and subsidence of the precipitate. Acetic acid does not succeed when used in place of hydrochloric acid. Alum is not decomposed, so as to render the alumina insoluble, during the process of baking. A small correction should be made in the amount of barium sulphate obtained when bread contains much common salt, which is always contaminated with some sulphates. Bread or flour may possibly be adulterated with calcium sulphate; it is, therefore, advisable to test a small portion of the dialysed liquid for lime with ammonic oxalate, ammonic hydrate, and acetic acid. E. W. P.

Estimation of Lead as Iodate. By C. Cameron (*Chem. News*, xxxviii, 145).—Lead may be estimated as iodate in the absence of hydrochloric acid, or alkaline chlorides, bromides, or iodides, lead iodate being far less soluble than even the sulphate is in alcohol. The lead iodate may be weighed, or it may be precipitated with a standard solution of iodic acid, the excess of which is estimated in the filtrate. The iodate solution must be standardised by means of a solution of pure lead nitrate. Hydrochloric acid rapidly dissolves lead iodate. L. T. O'S.

Detection of Mercury in Urine. By P. Fuerbringer (*Pharm. J. Trans.* [3], ix, 26).—In this method, 500—1000 c.c. of urine, acidulated and filtered, are heated to 60—80°, with 0·5 gram of brass shavings for 10 minutes; the shavings when dried are inserted into a tube, 0·8 cm. wide, and 15 cm. long; both ends of the tube are then narrowed to 0·1 cm., and the whole is heated to dark red heat, when the mercury volatilises and collects in the narrow portions of the tube. The iodine reaction is produced by introducing a small quantity of iodine into the tube. In this way ·00025 gram of mercury is easily detected. E. W. P.

Organic Analysis in the Wet Way. By J. A. Wanklyn and W. J. Cooper (*Chem. News*, xxxviii, 133—134).—A strongly alkaline solution of cane sugar is completely oxidised when evaporated to dryness with a solution of potassium permanganate, as is shown by the following equation:—

$$C_{12}H_{22}O_{11} + 10O_2 = 11H_2O + 4CO_2 + 4C_2O_3.$$

By estimating the oxalic acid formed, the amount of carbon converted into oxalic acid may be determined. The process is as follows:—1 gram of cane sugar, 3·9 grams of caustic potash, and 7 grams of potassium permanganate are dissolved in 150 c.c. of water, and evaporated nearly to dryness. The residue is dissolved in water, and the excess of permanganate titrated, the solution is filtered, and the oxalic acid estimated as calcium carbonate. By this method good results were obtained with grape sugar and with glycerin.

In the case of train oil and almond oil, it is necessary to evaporate quite to dryness to insure complete oxidation. Benzoic and lactic acid are readily attacked, acetic acid only slightly; alcohol in the cold yields acetic acid, without the formation of aldehyde. The acetic acid was estimated as barium salt, since it was not further oxidised.

Amyl alcohol yielded acetic acid, according to the following equation:—

$$C_5H_{12}O + O_7 = 2H_2O + 2C_2H_4O_2 + CO_2.$$

L. T. O'S.

Estimation of Mineral Oil or Paraffin Wax, when mixed with other Fats or Oils. By W. Thompson (*Chem. News*, xxxviii, 167).—The method consists in saponifying the oils with an alcoholic solution of caustic soda, and separating the unsaponified oil or wax with petroleum spirit. 200 parts of the oil are placed in a basin with 350 parts of an alcoholic caustic soda solution (strength, 9 per cent.

Na_2O), and boiled until the mixture begins to froth. 200 parts of methylated spirits are added to dissolve the soap, &c., 90 parts of sodium bicarbonate to convert any caustic soda into carbonate, and finally 500 parts of washed and ignited mortar sand. The mixture is boiled for a few minutes, and then the alcohol and water are distilled off from a water bath. The residue when cold is transferred to a wide-mouthed stoppered bottle, and shaken with petroleum spirit, the sand and soap are allowed to settle, and the spirit containing the wax and mineral oil is drawn off and filtered through asbestos. The residue of soap and sand is thrown on to a cloth, and the liquid pressed out. The petroleum spirit is distilled from the mineral oil at 100°, and the residue is transferred to a flask, with a hole blown in the side, which is fitted with a cork bearing a thermometer, and small piece of glass tubing; the whole is previously weighed, and the last traces of spirit are distilled at 220°; dry air is then blown through, and the whole is weighed.

Certain corrections have to be made, in consequence of oil capable of saponification containing small quantities of oil which cannot be saponified, and which are soluble in petroleum spirit. The correction in the case of Russian tallow amounts to ·64 per cent.

L. T. O'S.

Method of Separating and Determining Stearic and Oleic Acids produced by the Saponification of Fats. By J. DAVID (*Compt. rend.*, lxxxvii, 22, 1416—1418).—If a mixture of glacial acetic acid and water be gradually added to an alcoholic solution of *oleic acid*, a point is reached at which the oleic acid remains entirely dissolved, but is completely separated by the addition of one-tenth of a c.c. more of the acid. *Stearic acid* in alcoholic solution begins to precipitate as soon as the acetic acid is added, and is entirely insoluble in a mixture of alcohol and acetic acid, and that even in the presence of oleic acid. On this principle a method of analysis is founded. A litre of glacial acetic acid is mixed with a litre of water; 2·2 c.c. of this solution are added to 1 c.c. of pure oleic acid mixed with 3 c.c. of 95 per cent. alcohol, contained in a small tube graduated to tenths of a c.c., working with the solutions at 15°; this should cause no turbidity, but on adding another tenth of a c.c. a turbidity should appear, and 1 c.c. of oleic acid should rise to the surface. If this occurs, the solutions are mixed in the right proportions; if not, the proportions of alcohol and acetic acid must be varied until the precipitation occurs on the further addition of one-tenth of a c.c. of acetic acid. A mixture of alcohol and acetic acid in the proportions determined above is then prepared, and 1 or 2 grams of pure stearic acid in fine shavings are added to this liquid, in a wash-bottle provided with a small piece of sponge in its jet, to prevent undissolved stearic acid from escaping with the liquid; this bottle must be well closed when not in use, to prevent loss of alcohol by evaporation.

The sample of fatty acid used for analysis must contain the acids in the free state only, and must be in a very finely divided state; 0·95 gram is weighed into a small, well-stoppered tube, 15 c.c. of the mixture of alcohol and acetic acid are added, the tube is shaken several times, and then allowed to stand for 24 hours at a maximum temperature of 15°. The whole is then poured through a small filter, covered with a ground glass plate, and the stearic acid on the filter is washed three or four times with the alcohol-acetic liquid from the wash-bottle. The whole of the oleic acid will then be contained in the filtrate; the stearic acid is washed by a fine stream of cold water out of the filter into a tared platinum capsule. The capsule is heated until the stearic acid collects at the surface as an oily layer; after allowing this to cool and harden, the water is removed, and the cake of fatty acid is dried at 100°, or in a vacuum. Its weight then gives directly the quantity of stearic acid in 95 of fatty acid, that is, in 100 of the fat. F. C.

Glucose Reaction. By B. LINDO (*Chem. News*, xxxviii, 145—146).—When the yellow compound obtained by the action of nitric acid on brucine is dissolved in a caustic alkali, a solution is obtained, which gives a deep blue coloration with grape sugar, owing to its reducing properties, but scarcely any coloration with cane sugar. This reaction cannot, however, be used as a test for sugar in urine directly, since urine itself produces a change of colour more or less intense when heated with the test solution. If the urine be previously dialysed, this test may, it appears, be applied with certainty; this, however, requires confirmation. L. T. O'S.

Carbolic-Acid Powders. By A. H. ALLEN (*Analyst*, 1878, 285—288).—The following analyses show the composition of the residue left on igniting carbolic-acid powders. A is Calvert's powder; B a powder prepared by another manufacturer:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	Undetermined matter.	
A	67·4	28·0	traces	0·8	3·8	= 100·0 p.c.
B	68·6	26·3	traces	1·3	3·8	= 100·0 „

The following analysis shows the composition of a sample of MacDougall's powder (made by adding crude carbolic acid to the impure calcium sulphite, obtained by passing sulphurous acid gas over previously ignited limestone) after extraction of the carbolic acid by ether:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	SO_2.	SO_3.	CO_2,H_2O and undetermined matter.	
2·4	3·4	traces	46·5	0·3	7·5	29·2	10·7	= 100·0 p.c.

The extraction of the carbolic acid was probably incomplete, as the analysis, subsequently made, shows free lime, and the powder was distinctly alkaline. As the carbolic acid in the siliceous products is wholly in a free state, it is readily extracted by ether or other solvents. It is, however, difficult to drive off the solvent liquid afterwards without loss of some of the carbolic acid itself by volatilisation. Processes for the determination of carbolic acid by conversion into tribromophenol or sulphocarbolic acid are unsuited for the assay of carbolic powders, as they ignore the presence of tar-oils and give inaccurate results where applied without correction to mixtures containing cresol. A more convenient process is that based on the distillation of the powder and collection of the carbolic acid, &c., volatilised (*Vincent's Manufacturing Chemistry*, vol. i, 633).

Good carbolic-acid powder should contain 12 to 15 per cent. of crude carbolic acid. The distillation process fails when applied to a powder made by adding carbolic acid to slaked lime. Such powders are of very little value for disinfecting purposes. Carbolic acid used in the preparation of disinfecting powders is frequently largely adulterated. It chiefly consists of cresol, and is frequently mixed with a large percentage of tar-oils. The detection of these impurities and their separation is based on their insolubility in caustic alkalis.

A useful test of the value of carbolic powder may be made as follows:—Mix 25 grains of each powder with 1 ounce of flour, and then gradually add 10 ounces of water, mix well in the cold, then raise the liquids to boiling, and pour out each paste into a glass to set. Leave the pastes exposed to the air, and the value of the powders as antiseptics will be indicated by the time which elapses before mildewing occurs, and the rate and manner in which it progresses.

D. B.

Morphine Reactions. By D. LINDO (*Chem. News*, xxxviii, 65—66).—1 part of crystallised copper sulphate is dissolved in 10 parts of water, and solution of ammonia added cautiously and with active stirring until the precipitate is just dissolved. To ascertain if this solution is fit for the above reaction dissolve 2 grains morphine chloride in 1 ounce of distilled water; place some of this in a test tube, add a few drops of the test fluid, and shake the vessel slightly. If a precipitate or permanent turbidity is observed, the test fluid requires a little more ammonia, which should be added in small quantity, as an excess of ammonia prevents the test from acting. When a few drops of a properly prepared test fluid are added to a neutral solution of morphine salt of the above strength, and the tube is slightly shaken, no cloudiness will be observed, but the fluid assumes a magnificent emerald-green colour either immediately or after a short time. Phenol is the only other colourless organic compound, which has been met with as yet, which affords a similar colour reaction.

D. B.

A direct Method for determining the Calorific Power of Alimentary Substances. By J. A. WANKLYN and W. J. COOPER (*Chem. News*, xxxviii, 134).—The authors have so modified Forchhammer's process as to make it of practical use. It consists in distilling a given volume of the solution of the substance under examination with a strongly alkaline solution of potassium permanganate, and titrating the excess of permanganate in the residue, having previously acidified it. The reagents consist of (1) a solution of potassium permanganate containing ·4 mgrm. of active oxygen per c.c.; (2) standard ferrous sulphate solution, 1 c.c. of which corresponds to 1 c.c. of the permanganate solution; (3) a 5 per cent. potash solution, and (4) sulphuric acid containing 1 vol. of acid to 9 vols. of water.

To the water to be examined is added 5 c.c. of potash solution and 5 c.c. of potassium permanganate, and the whole is rapidly distilled from a retort. If the permanganate is completely reduced, a second quantity is added, and if necessary a third. When 900 c.c. have distilled over, the residue, which must contain unreduced permanganate, is acidified, and a measured quantity of the standard iron solution is added in excess, which is titrated back with the permanganate solution. From these data the amount of oxygen used by the water may be calculated.

L. T. O'S.

Milk Analysis. By LEHMANN (*Landw. Versuchs. Stat.*, xxii, 67—68).—Clay plates are heated to 100° C. or higher, and after cooling are quickly moistened whilst held obliquely by means of a thin jet of water; they are then placed on a sufficiently wide vessel containing a thin layer of concentrated sulphuric acid. The milk, previously diluted with an equal quantity of water, is carefully passed on to the centre of the plate from a small wash-bottle, and is covered with a glass. About 9 to 10 grams of milk is sufficient for exact results. In from one to two hours the casein and fat can easily be removed by means of a sharp horn spatula, and dried at 105° and weighed. The dried mass is then placed on a weighed filter, moistened with ether, finely pulverised in a glass mortar with a little alcohol, treated with ether, and filtered. The solution evaporated to dryness gives the fat, the residue dried gives the casein with ash. The ash is separately determined and subtracted. Casein results are 0·2 per cent. higher than those obtained by separating with acetic acid. J. T.

Presence of Non-coagulable Nitrogen Compounds in the Cereals. By G. W. WIGNER (*Analyst*, 1878, 288—290, and 303—306).—Church and others have pointed out that the estimation of nitrogen for the purpose of calculating the albuminous matter present in vegetable-products, is not quite trustworthy as a true measure of albuminous matters. All the cereals, as well as roots, contain a considerable proportion of nitrogen combined in other forms, which are not capable of being coagulated by acid, and which, judging from inference, have very little flesh-forming property. This non-coagulable nitrogenous matter exists mainly in the husks or bran of the cereals; the flour, when perfectly freed from husk, containing a comparatively small proportion of it. It is evident, therefore, that this may have led to some erroneous estimates of the relative feeding value of the whole meal as compared with flour. It is quite clear that, as regards whole meal, the nitrogen determination is not to be relied on as giving an accurate estimate of the amount of flesh-formers present. A large number of nitrogen determinations were made with wheat, barley, and oats. Besides this the meals were treated with a solution of carbolic acid, faintly acidulated with a few drops of dilute nitric acid, and after warming, standing, and filtering, the insoluble residue was washed on the filter with carbolic acid solution. Since the true albuminoïds are coagulated by this process, the residue on the filter will contain them all, whilst the nitrogenous matters present in other forms pass through with the filtrate. Combustions made with the residue left on the filter showed that on an average 17·7 per cent. of the total nitrogen is present in wheat in such a form that it is not capable of being coagulated by carbolic acid; 17·6 per cent. is also present in the same form in oats, and 14·7 per cent. in barley.

The author therefore concludes that the flesh-formers present in the whole meal of the cereals have been over estimated to the extent of from 15 to 20 per cent., and that the residual nitrogen present in other forms is not equally valuable as a flesh-forming constituent.

It becomes of great importance to find in what state of combination this residual nitrogen does exist. In the case of barley the largest proportion of nitrogen, in the form of nitrates and nitrites, is ·050 per cent., equal to ·194 per cent. nitric acid, and the lowest proportion yet obtained is ·033, equal to 1·62 per cent. nitric acid. These figures show that the nitrogen, in the form of nitrates and nitrites, is part only of the residual quantity. In the first case, then, non-coagulated nitrogen was ·140 per cent., and the proportion of it present as nitrates and nitrites was therefore 36 per cent., while in the second case the non-coagulated nitrogen was ·061 per cent., and the proportion of it present as nitrates and nitrites was 54 per cent.

In the second part of his paper the author describes the manner in which he obtains the meal in a form suitable for analysis. Although it is impracticable to grind or dress a small sample in the same perfect manner as a miller dresses his flour, it is thought that this does not interfere sensibly with the comparative results.

The coagulation of the true albuminoïds is carried out exactly as described by Church (*Laboratory Guide*, 1877, Ed. IV). As to the filtrate, a portion may be taken for the determination of nitrogen as nitrates and nitrites, provided, of course, that nitric acid has not been used for acidifying the paste. As to the other nitrogenous constituents which are not coagulated, all that can be said at present is that part is present as alkaloïd and part also as gluten.

The following table shows the results obtained by the combustion of 15 samples of whole meal from wheats, together with the results obtained from the same samples, after treatment with carbolic acid as already described, and the ratio shown to exist between the true albuminoïds and the albuminoïds calculated from the total nitrogen found by the combustion process:—

TABLE I.—*Wheat.*

Nitrogenous matters present in the whole meal of 15 samples of wheat compared with the coagulable nitrogenous matters.

Nitrogenous matters = N × 6·33. All results in percentages.

Mark.	Nitrogenous matter in whole meal.	Nitrogenous matter coagulated by carbolic acid.	Nitrogenous matter not coagulated.	Percentage of true gluten calculated on total nitrogenous matter.
A	11·54	10·14	1·40	87·9
B	9·14	7·39	1·75	80·9
C	8·53	7·89	0·64	92·5
D	9·41	8·65	0·76	91·9
E	9·52	6·27	3·25	65·9
F	10·66	8·15	2·51	76·4
G	9·40	7·89	1·51	83·9
H	9·28	7·52	1·76	81·0

Mark.	Nitrogenous matter in whole meal.	Nitrogenous matter coagulated by carbolic acid.	Nitrogenous matter not coagulated.	Percentage of true gluten calculated on total nitrogenous matter.
I	9·53	7·02	2·51	73·7
K	9·15	7·27	1·88	79·4
L	9·15	6·77	2·38	74·0
M	11·28	10·15	1·13	90·0
N	8·03	7·65	0·38	95·3
O	10·02	7·64	2·38	76·2
P	13·79	11·01	2·78	79·8

The following table gives the results of the nitrogenous matter present in the bran of 15 samples of wheat compared with the coagulable nitrogenous matters:—

TABLE II.—*Wheat.*

Nitrogenous matters $= N \times 6·33$. All results in percentages.

Mark.	Nitrogenous matter in bran.	Nitrogenous matter coagulated by carbolic acid.	Nitrogenous matter not coagulated.	Percentage of true gluten calculated on total nitrogenous matter.
A	13·42	5.69	7·73	42·4
B	13·60	8·10	5.50	59·6
C	11·77	—	*	—
D	8·67	3·54	5·13	40·8
E	7·43	5·69	1·74	76·6
F	9·33	8·10	1·23	86·8
G	10·57	9·49	1·08	89·8
H	11·01	7·72	3·29	70·1
I	11·65	10·25	1·40	88·0
K	10·05	6·46	3·59	64·3
L	11·24	7·46	3·78	66·4
M	10·76	8·48	2·28	78·8
N	8·23	6·71	1·52	81·5
O	9·24	4·81	4·43	52·1
P	15·66	8·73	6·93	55·7

Two points at once attract attention here; first, the great difference between the coagulable and non-coagulable albuminoïds, and secondly, the difference between this ratio and that found when the whole meal was similarly treated.

D. B.

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* Spoilt in analysis.

Technical Chemistry.

Extraction of Iodine and Bromine from Kelp. By R. GALLOWAY (*Chem. News*, xxxviii, 146).—The author discusses the disadvantages of Wollaston's process for the extraction of iodine and bromine from kelp, and proposes to use chlorine as a liberator of these bodies instead of manganese dioxide and sulphuric acid.

The process proposed by the author is as follows:—After extracting the potassium chloride, the kelp liquor is exactly neutralised with sulphuric acid, and in a small sample the amount of chlorine water necessary to form iodine pentachloride is determined. To the bulk of the liquor one-sixth of the relative quantity of chlorine water which was required by the small sample is added. This liberates the iodine, which is removed, and the amount of chlorine-water for the liberation of the bromine determined, and one-half the relative quantity is added, which liberates the bromine. If the solution should be rendered too dilute by precipitating all the iodine and bromine with chlorine water, a portion might be precipitated by the gas and the remainder with the solution. L. T. O'S.

New Mineral White Pigment. By T. L. PHIPSON (*Chem. News*, xxxviii, 105).—Whilst experimenting on some of the artificial silicates which are remarkable for their brilliant white colour, the author learnt that Mr. T. Griffiths, of Liverpool, had obtained a new mineral white, the basis of which was sulphide of zinc; and on submitting this new product to a careful examination, the author found that it not only surpassed the old zinc white, but that it was superior in every respect to carbonate of lead itself. It is obtained by precipitating either chloride or sulphate of zinc by means of a soluble sulphide—sodium, barium, and calcium sulphides have all been used for this purpose—and precautions are taken lest any iron that may be contained in small quantities as an impurity in the zinc solution, should be precipitated with the sulphide of zinc. The precipitate, being collected and dried, is transferred to a furnace, where it is calcined, and after careful stirring it is raked out, while quite hot, into vats of cold water, when it is levigated, and afterwards collected and dried. The result is a white pigment of exquisite beauty; its covering power when mixed with oil is greater than that of any substance hitherto discovered, being about 25 per cent. higher in this respect than that of the same weight of pure carbonate of lead. According to the author's analysis, this new product consists of an oxysulphide of zinc, the composition of which varies somewhat according to the duration of the calcination and the exact degree of heat attained. The best product appears to correspond very closely with the composition $5ZnS + ZnO$.

D. B.

Toughening of Glass. (*Dingl. polyt. J.*, ccxxix, 57—66).—The discovery of toughened glass in 1875 by R. de la Bastie, raised great expectations; but these have not as yet been realised, the properties of toughened glass not having caused it to supersede ordinary glass.

It is well known that toughened glass is obtained by a process of sudden cooling, which may be effected in various ways, and by the use of different cooling agents. The resulting change is of a purely physical nature, the chemical composition of the glass remaining unaltered. The suddenness with which the softened mass passes over into the solid condition gives rise to a state of molecular tension in glass, which gives the latter its specific properties. The chemical and physical properties of glass used for toughening purposes are of great importance. Badly fused or ill-refined glass always cracks in the cooling bath, whilst the presence of basic or acid constituents facilitates devitrification and hinders the success of the toughening process. The temperature of the cooling bath varies with the fusing point of the glass to be toughened, and also depends on the outer form and the thickness of the sides of the vessel under operation. The cooling effect of a toughening bath is regulated by the specific conducting power of heat of the substance forming the bath, good conductors requiring higher temperatures than bad conductors. Such baths may consist of fatty substances, oil, glycerin, paraffin, hydrocarbons, concentrated saline solutions, and readily fusible metallic alloys. Water cannot be employed; all baths must be absolutely free from the latter. Fat or oil baths are not only very expensive, but also give rise to the danger of fire, sudden alteration of temperature, and other defects. Steam has the property common to fat baths of being applicable at different temperatures, and has the advantage that such baths retain the same temperature during the whole process. The cooling action of steam baths on red-hot glass may be regulated, apart from a higher or lower temperature, by using superheated, saturated, or supersaturated steam. Solid bodies have also been used for toughening purposes.

The resistance of glass toughened by oil is said to be equal to 601 kilos., toughened by means of steam, 700 to 1,100 kilos., whilst ordinary glass possesses a tenacity of 220 kilos. per square centimeter. Bottles of toughened glass stand a pressure of 52 atmospheres, ordinary glass bottles only 39 atmospheres. It also bears sudden alterations of temperature without cracking.

When ordinary glass is, after fusion, cooled slowly and investigated optically, no important appearances are observable, a fact which proves that no irregularity in the structure has taken place. Toughened glass, on the other hand, gives coloured lines, which vary in character and intensity with the form, the thickness, and the toughness of the glass.

With regard to the various theories proposed to account for the toughening, the author explains that owing to incorrect observations the opinion was held for some time that toughened glass had a higher specific gravity than common glass. Hence it was thought that by the sudden change from the liquid to the solid state the expansion of the glass was hindered, the product becoming specifically heavier. On this fact all other characteristic properties were based. Recent investigations, however, have shown that the specific gravity of toughened glass is less than that of slowly cooled glass.

A toughened glass plate which resists the fall of heavy weights, provided they drop on the centre of the plate, breaks very easily by a mere blow with an instrument against its sides or edges. When the edge of an untoughened glass is struck against some object, the former often breaks only partially and is not altogether useless; toughened glass, however, is completely destroyed under the same conditions. For this reason the manufacture of toughened glass decanters, beakers, or bottles cannot be recommended.

In conclusion it is mentioned that although no satisfactory observations have been made regarding the duration of the toughness of glass, it is nevertheless probable that toughened glass loses its peculiar properties in the course of time. D. B.

Electro-deposition of Cobalt. By A. GAIFFE (*Compt. rend.*, lxxxvii, 100).—Cobalt as deposited by the electric current is preferable to iron and nickel as a protective surface to clichés, &c., as it does not oxidise like iron, and when necessary it can be readily dissolved by dilute acids, which do not attack the copper under-surface. For the electro-deposition of cobalt on copper the author employed a neutral solution of the double sulphate of cobalt and ammonium. The positive electrode is connected with a platinum or preferably with a cobalt plate, and by passing a regular current through the solution for four hours an adhering and regular deposit of white metallic cobalt, 0·025 m.m. in thickness, was obtained.

Becquerel (*ibid.*, p. 130) claims to have already described a method similar to the above in a paper published in 1862 (*Compt. rend.*, lv, 18). A. J. C.

Sulphur and Phosphorus in Iron. By S. KERN (*Chem. News*, xxxviii, 145).—The author gives an example showing the unequal distribution of sulphur and phosphorus in iron, by analysis of shearings taken from different parts of a bar 44 inches in length. L. T. O'S.

Analysis of a Remarkable Iron Slag. By J. R. SANTOS (*Chem. News*, xxxviii, 108).—This slag—an accidental product from a puddling furnace at Herbert's Park Iron Works, Bilston, Staffordshire—presented a jet black colour, was opaque in the thinnest splinters, of unusually high lustre, between vitreous and pseudometallic, reflecting like a mirror the images of surrounding objects, with perfect conchoïdal fracture and knife-like splintery edges; sp. gr. 2·89; hardness nearly 7. Analysis:—

SiO_2.	Al_2O_3.	FeO.	Cu_2O.	CaO.	K_2O.	Na_2O.	
47·67	26·36	21·99	0·19	0·79	1·71	1·12	= 99·83

These figures lead approximately to the formula of the disilicate, $Al_4Fe_3Si_6O_{21}$, corresponding to $H_6Si_2O_7$. D. B.

Influence of Heat on the Structure of Steel. By W. METCALF (*Dingl. polyt. J.*, ccxxix, 92—93).—In relation to Matthieu Williams's contributions to the theory of steel (*ibid.*, ccxxviii, 543), the author gives the following data, in regard to the hardening of steel. Any difference in temperature which suffices to effect a change in the colour of the metal produces a difference in the grain, and latter causes an interior expansion, which is accompanied frequently by the formation of cracks in the metal. If the temperature is sufficiently high to form a grain which is coarser than that possessed by the original substance, the hardened metal becomes brittle, is liable to crack, and shows but little resistance at its edges. If the temperature on the other hand is merely high enough to harden the metal without altering the grain, the steel has been refined in a satisfactory manner. It is stronger than the original metal, its edges being tough and cutting. Such temperatures are the most suitable for the preparation of boring or cutting instruments.

It is known that hardened steel may be annealed by heating it, and then cooling it slowly; but the product never possesses the original firmness. It will be seen from the above that every instrument made of steel, if it is first heated and then cooled even with the utmost care, is liable to have cracks in it or suffer alteration of form, if its separate parts have not been previously exposed to a regular temperature. Moreover, every instrument of steel will be rendered useless for the purpose for which it was intended if it has not been heated to the corresponding temperature.

Langley's experiments coincide with those of the author, and are worthy of notice, as they give some interesting relations regarding the proportions of the densities of hardened and unhardened steel. It is shown that (1) the rolling process increases the specific gravity; that (2) the hardening operations decrease the same; and that (3) the refining methods do not increase the specific gravity. D. B.

Mending Platinum Crucibles. By T. GARSIDE (*Chem. News*, xxxviii, 65).—The author found that platinum being "weldable," crucibles of this metal might be repaired in this manner. A mould was made of plaster of Paris, which served admirably as an anvil. A piece of moderately-thin platinum foil was laid over the hole, and the flame of a blowpipe directed upon the spot, the part where the hole was having previously been rubbed with sea-sand until perfectly clean and bright. On gently tapping with a pair of scissors, which served as a hammer, the two pieces of platinum united perfectly and made a neat joint. Although the dish has been used for all kinds of purposes since, the union is as good as ever. Platinum wires are very easily joined in this manner. D. B.

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ERRATA.

The asterisk in the second column indicates that the line is counted from the bottom.

Page.	Line.	Error.	Correction.
219	6*	Sulphuric	Sulphinic
382	7	3Ᵽ	3Ᵽ3
392	18	Petroleum?	Coal-tar naphtha
553	1—3	c.c. H_2O_2 vapour in 1000 c.c. of air	c.c. H_2O_2 vapour in 1000 cubic meters of air
—	14	0·17 c.c. H_2O_2 per litre	0·25 c.c. H_2O_2 vapour in 1000 cubic meters
568	27	Oxygen for Sulphur	Sulphur for Oxygen
698	11	combinations	carbon-atoms
700	3*	$\frac{K}{1·25}$	$\frac{I}{1·25}$
701	2	$\frac{Br}{1}$	$\frac{Br_2}{1}$
704	1	1·4 c.c. H_2O_2 per litre of air	1·4 c.c. H_2O_2 vapour in 1000 cubic meters of air
922	7	kilos	kilns
944	20*	Madriach	Modriach
973	4	monobromisopropyl	monobromisopropylbenzene

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